

ABSTRACT

Title of Document: EVALUATION OF LEACHING PROTOCOLS
FOR THE TESTING OF COAL
COMBUSTION BYPRODUCTS

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Beneficial reuse of coal combustion byproducts requires an evaluation of metal leaching potential. Reuse of high carbon fly ash in highway embankment construction was evaluated using different soil-fly ash mixtures and three common leaching tests: the water leach test (WLT), the Toxicity Characteristic Leaching Procedure (TCLP), and the column leach test (CLT). The effect of test methodology and pH on Cu, As, and Cr leaching was examined. TCLP concentrations for Cu and As exceeded those from WLTs in the majority of mixtures due to lower pH conditions, while Cr was higher in the WLT for alkaline fly ash mixtures. Peak CLT concentrations were higher than TCLP and WLT concentrations for the majority of mixtures, but usually decreased rapidly, suggesting that leachate concentrations might exceed regulatory limits, but only for a short time. Based on these results, a combined WLT and CLT leaching protocol for testing fly ash mixtures is presented.

EVALUATION OF LEACHING PROTOCOLS FOR THE TESTING OF COAL
COMBUSTION BYPRODUCTS

By

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Chapter 1: Introduction

More than 50% of the electricity demand in the United States is met from coal-fired power plants, which burn over 1 billion metric tons of coal annually to provide electricity to homes, businesses, and industries (Kim 2006). This generation of electricity results in production of coal combustion by-products (CCBs) that require proper handling and disposal or beneficial reuse. For example, fly ash, one of the main types of CCBs, is the collected particulate matter from the exhaust gases of coal power plants. The CCB disposal problem has been exacerbated by increases in electricity demand, which have led to higher rates of coal burning, producing more CCBs. This coupled with the high levels of hazardous metals in CCBs and the large landfill space required, has resulted in CCB disposal receiving increasing attention. Correspondingly, there have been increased efforts to research and develop new, more sustainable disposal methods for CCBs that do not compromise the well-being of the environment or endanger human health.

Disposal of CCBs presents an environmental challenge due to both environmental and human health concerns. The majority of CCBs have traditionally been placed in landfills, which may adversely affect both terrestrial and aquatic resources. In addition, decreases in available areas suitable for new landfill space has magnified the need for the development of alternative disposal and management options. For instance, 1.7 million tons of fly ash were produced at various facilities in Maryland in 2008, and nearly 745,000 tons of this ash were reused in beneficial applications throughout the state, corresponding to about 44% of the generated ash (MDE 2008). This quantity of reused fly ash represents a significant portion of fly

ash that would otherwise be disposed of in a landfill, taking up large areas of space. However, the risk of contaminating groundwater supplies and harming wildlife from soil and/or water contamination are examples of issues that need to be addressed before beneficial reuse of fly ash can become widespread.

A common beneficial use of fly ash has been as a concrete additive due to its natural pozzolanic properties. However, changes in the U.S. Clean Air Act requiring the use of low sulfur and nitrogen oxide emission burners has resulted in CCBs with higher carbon contents. High carbon fly ash is problematic in concrete applications because it absorbs the air-entraining additives that are added for increasing the porosity of the concrete (Cetin 2009). As a result, there is currently a renewed emphasis on incorporating suitable CCB into construction activities. One area of CCB reuse that has received much attention is the construction of highways and roadway embankments. Both the reduction in construction materials required and large volume of fly ash that can be recycled make embankment construction an ideal candidate for beneficial fly ash reuse. Nevertheless, despite the advantages of reusing CCBs, potential impacts on groundwater quality still remain an issue when these by-products are used in construction applications.

Two major environmental concerns related to the reuse of fly ash in construction applications, such as the building of roadway base layers or highway embankments, are leaching of heavy metals and the consequences from changes in pH. Heavy metals such as As, Cr, Cu, Pb, Se, Cd, and Zn can be present in fly ash in levels up to several hundred parts per million (Bin Shafique et al. 2002, Ram et al. 2007, Shah et al. 2008). Leaching of metals from fly ash-amended materials has the

potential to contaminate nearby natural waters. Although metal leaching can occur at the parts-per-billion scale, the potential to accumulate in the natural environment and various means of transport throughout ecosystems require investigation into the unintended effects of beneficial fly ash reuse. There have been numerous studies looking at heavy metal leaching from fly ash mixtures, and the general consensus is that both fly ash composition and pH have important effects on leaching behavior and speciation of metals (Fytianos et al. 1998, Bin Shafique et al. 2007, Jegadessan et al. 2008, Jo et al. 2008, Morar et al. 2010).

Work by Shah et al. (2008) showed that metal concentrations in coal fly ash collected from an Australian power plant were roughly 2-4 times the original concentration in the source coal. This was attributed to the loss of mass on ignition from the organic carbon being oxidized to carbon dioxide in the combustion process. Ram et al. (2007) also state that metal can become concentrated during the coal burning process by factors of 4-10. For example, Shah et al. (2008) measured 0.857 mg/kg of Cr(VI) in a fly ash compared to 0.065 mg/kg in the source coal. Changes in metal speciation may also occur during and after the combustion process. This is illustrated by the study of Shah et al. (2008), which showed that a fly ash had 90% of As present in the As(V) form compared to 65% in original coal material. This is important because it could also have implications for leaching behavior, and it is widely known that certain species of metals are more toxic than others. For example, As(III) is 50 times more toxic to humans than As(V) while Se(IV) had higher reported toxicity than Se(VI) (Shah et al. 2008).

The pH of the leachate from a fly ash-containing soil has a strong influence on many other natural processes that occur within the soil matrix. The speciation of metals, availability of nutrients such as nitrogen and phosphorus, soil weathering, and partitioning (and therefore transport) of pollutants are all affected by changes in pH. With respect to partitioning processes, the sorption, precipitation, and dissolution processes that largely control metal leaching behavior are all pH dependent, with dissolution of metal-containing minerals seen under acidic pH, while precipitation and complexation dominate at higher pH values (Jegadessan et al. 2008, Morar et al. 2010). The mobility and toxicity of heavy metals are related to both the amount of these metals that enter the environment from leaching processes and the metal species present.

Coupled with the increased interest in the beneficial reuse of CCBs has been an increase in the development of regulations governing their disposal and use. In particular, concerns with environmental health and human safety have prompted agencies across the country to begin to devise programs outlining proper methods to handle and dispose of fly ash and other CCBs. While the U.S. EPA has been working to create federal regulations for CCBs since 2000, there have been no laws passed. This has resulted in an opportunity for states to devise their own standards while federal regulations are being proposed. For instance, the Maryland Department of the Environment (MDE) created the Regulation of Coal Combustion Byproducts legislation (COMAR 26.04.10.00) to address the issue of safe CCB handling, processing, disposal, and reuse, and to develop procedures for disposing of or reusing fly ash in beneficial applications. Also included are activities that are prohibited

based on issues of water, air, and human health quality concerns. One of the primary topics of the regulations is the risk associated with heavy metal leaching from fly ash mixtures used in construction projects, such as highway embankments.

Therefore, despite the advantages of reusing CCBs, potential impacts on groundwater quality remain an issue when these by-products are used in construction applications. Currently, the MDE requires that the CCBs or other industrial by-products be subjected to the EPA Toxicity Characteristic Leaching Procedure (TCLP) test to determine if the material can be used in field construction applications without causing groundwater and surface water contamination. However, concerns have been raised by various interested parties about the use of this testing methodology, as the testing conditions are typically harsher than those encountered in the field, the test is not material or site specific, and it neither represents the actual leachate produced in the field nor simulates a site-specific transport condition (Baba and Kaya 2004, ASTM D3987-06, Ram et al. 2007). Furthermore, the test method is used to determine if the material is hazardous or not; however, more than 15 years of research based on TCLP and column tests clearly shows that the CCBs are generally non-hazardous (Creek and Shackelford 1992, Kyper 1992, Chichester and Landsberger 1996, Edil 1998, Ghosh and Subbarao 1998, Qiao et al. 2006, Bin Shafique et al. 2006).

Concerns with the use of the TCLP test has led to interest in alternative ways of evaluating leaching of fly ash-soil mixtures. One alternative is the use of field lysimeters (Ahmed et al. 2010); however, their high costs and long testing duration stand as barriers to their widespread use. Furthermore, the composition of fly ash can

vary even within daily batches. Thus, there is a demand for methodologies that can appropriately evaluate leaching potential using more standard laboratory equipment and do so at more frequent intervals. This would provide fly ash producers with more real-time data and aid in better selection of fly ash disposal or reuse options.

Similarly, regulators at the state and federal level would also benefit from having a standardized way to easily gage the expected leaching behavior of a fly ash mixture, and could use this information as a tool in accessing the feasibility of beneficial reuse of fly ash and other CCBs.

Clearly, there is a need to determine the most appropriate leaching test for evaluating the potential environmental impacts of CCBs when beneficially used, such as in highway construction applications. The experimental conditions of the selected leaching test must realistically predict leaching, thereby helping regulators and power plant companies minimize risk. The selected method must also be cost-effective and timely, and avoid misleading results, which would hinder efforts to promote increased reuse of CCBs. For example, Baba and Kaya (2004) found that ASTM batch leach tests indicated a fly ash waste was non-toxic whereas TCLP results showed elevated leachate metal concentrations and a toxic classification. Therefore, the primary objective of this project was to compare the methodologies and leaching results of three leaching tests commonly used today: the ASTM water leaching test (WLT), the TCLP test, and the ASTM flow-through column leaching test (CLT). Both batch and column tests were run to understand how the testing conditions influence the leaching results. In addition, the tests were conducted on different mixtures of soils and fly ashes, and the concentrations measured in each test were compared with those

obtained by other researchers as well to the state and federal regulatory limits. The effect of pH on leaching was also examined through a series of batch-scale leaching tests. The results of these tests were used to provide recommendations on how to select leaching tests that give consistent leachate concentrations most representative of the field leaching conditions.

An initial survey of the metals present in the tested fly ashes was used to select the metals monitored in the three types of leach tests. The criteria for selection were that the metal must: (1) be present in relatively high levels in the fly ash, (2) be a concern from an environmental or human health perspective, and (3) be accurately measured on available instrumentation. Based on these criteria, chromium, copper, and arsenic were selected for study in this project. Chromium and arsenic are hazardous to human health which is reflected in their inclusion in the U.S. EPA's Safe Drinking Water Act as Maximum Contaminant Levels (MCLs). Copper was chosen because of its known toxicity to fish and other aquatic life (Horne and Dunson 1995). Although arsenic is a metalloid, it is referred to as a metal through this study. These metals also allowed anionic and cationic species to be examined across a wide pH range.

The work is presented in the following chapters. Chapter 2 outlines the materials used in this study and the procedures followed in performing the preliminary work and leaching tests. The results from the different leaching tests on the soil-fly ash mixtures are presented and discussed in Chapter 3. Chapter 4 provides some practical implications of the leaching test results, including an

integrated protocol for the testing of fly ash-soil mixtures. Lastly, Chapter 5 contains a summary of the results and the main conclusions from this study.

Chapter 2: Materials and Methods

2.1 Materials

Mixtures of two fly ashes and two soils were used to evaluate the effect of a range of chemical and physical properties on metal leaching. Fly ashes were added to the soils at 10% and 20% by weight to bracket the range most commonly applied in on-site embankment construction. Both soils underwent testing to determine several basic geotechnical properties, including specific gravity (ASTM D859), pH (ASTM D4972), loss on ignition (LOI) (ASTM D7848-08), and Atterberg limits (ASTM D318). Sieve analyses were also performed on the soils to classify them according to the Unified Soil Classification System. Total elemental analyses (TEA) were performed on soils and fly ashes at the University of Wisconsin Soil Testing and Plant Analysis Laboratories by using a Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer. The results from the TEA are provided in Table 2.1. Table 2.2 provides a summary of physical and chemical properties of the materials used in this study. The classification of the soils showed that they are sandy soils, with varying percentages of clay particles. The first soil, designated as Soil C, has a higher fines (clayey) content while the sandy soil (Soil S) is more uniformly graded.

The fly ashes used in this study, Brandon Shores (BS) and Columbia (C), were provided by power plants in Maryland and Wisconsin, respectively. These represent a non-cementitious (low calcium oxide) fly ash (BS) and self-cementitious (high calcium oxide) fly ash (C). The higher calcium content reported in the TEA (14.4%) for the Columbia fly ash provides its self-cementitious property upon

hydration. Specifically, a higher calcium level is indicative of higher levels of calcium oxide, which reacts with water to form hydroxide ions. This is reflected in the more alkaline pH of 11.9 of the C fly ash compared to the BS fly ash pH of 8.8

Two extraction fluids were used in the leaching tests described below. In the batch water leach tests (WLTs) and column leach tests (CLTs), the leaching solution was a 0.02 M NaCl solution. The ionic strength of the solution was selected to simulate the ionic strength of groundwater that would be flowing through a constructed embankment (Morar et al. 2010). Sodium chloride was expected to have minimal effect on the leaching process and the molarity was selected to be consistent with that of similar studies (Bin Shafique et al. 2007 and Morar et al. 2010).

Extraction fluid #1, an acetate buffer solution, was used as the extraction solution in the TCLP tests. The solution was selected as outlined in EPA Method 1311 (U.S. EPA SW-846) on the basis of the pH of the soil-fly ash mixture after heating and addition of HCl. A detailed description of the preparation and selection of these extraction solutions is provided in Appendix B.

2.2 Sample Preparation

As part of the specimen preparation, the soils were oven dried at 120°C for a minimum of 24 hours to remove all moisture. This was necessary to accurately assess the water content during preliminary compaction tests and achieve proper moisture content in the final compacted mixtures. For the column tests, the soils were sieved using a No. 4 sieve (4.76 mm). A total of 12 different mixtures were prepared for testing. For the batch tests, additional sieving through a No. 12 (2.00 mm) sieve

was done to account for the smaller size of the testing equipment. No sieving of fly ashes upon shipment was necessary due to their relatively fine grain sizes. To maximize the degree of homogeneity, the soil-fly ash mixtures were mixed by hand and using metal spoons in five-gallon buckets. Mixing was carried on for a minimum of 5 minutes or until the mixture appeared well mixed. Mixture samples were labeled using the following format: soil (C for clayey or S for sandy) – fly ash used (C for Columbia or BS for Brandon Shores) – percent fly ash by mass (10 or 20). For example, sample S-BS-10 contained a mixture of sandy soil plus 10% (by mass) BS fly ash. Table 2.3 provides a complete list of mixtures used in this study.

2.3 Leaching Test Procedures

2.3.1 Water Leach Test (WLT)

WLTs were performed on 12 mixtures according to ASTM D3987 with two modifications. One, the size of the extraction vessel was downsized from 2 L to a 60 mL centrifuge tube to fit the equipment available in the laboratory as previously done by Morar et al. (2010). Two, a 0.02 M NaCl leaching solution was used instead of the deionized water specified by the standard method. This background electrolyte produced conductivities more representative of actual embankment situations. To initiate the test, a 2.5-gram aliquot of the sample mixture was transferred to an acid-washed centrifuge tube, and 50 mL of leaching solution were added, corresponding to a 20:1 liquid-to-solid ratio. The tubes were rotated at 29 rpm for 18 hours \pm 2 hours using an end-over-end tumbling mixer (ATR Corporation) to allow for equilibration.

After rotation, the WLT samples were then placed in a centrifuge (Beckman Allegra) at 2000 rpm for 10 minutes to separate the liquid leachate and solid phases. Additional solids separation was achieved by filtering the resulting leachate through a 0.2 μm membrane filter (Pall Corporation) using a 60-mL LuerLock syringe fitted with a 25-mm Easy Pressure filter holder. Electric conductivity and pH measurements were taken for all samples immediately after filtration. The samples were then acidified to $\text{pH} < 2$ by adding roughly 0.5 mL of concentrated trace metal grade HNO_3 . All samples were refrigerated at 4° C until metal analysis could occur.

A second series of WLTs were performed to examine the effect of pH on the leaching behavior of the fly ash-soil mixtures. These tests followed the WLT procedures described above, except the 0.02 M sodium chloride extraction solution was buffered at target pHs of 7 and 9. The biological buffers, BES and CAPSO (> 99% Sigma Aldrich) were used to maintain a pH of 7 and 9, respectively, due to their minimal interference with metals. The buffered solutions were prepared by dissolving 2.13 grams of BES and 2.47 grams of CAPSO in 100 mL of the original WLT extraction fluid. The pH was measured and adjusted to the target value by the addition of 4 N NaOH during constant mixing by magnetic stirrer. Preliminary tests were conducted to confirm that the addition of the buffers provided adequate buffering capacity. Specifically, pH measurements were performed on WLT samples every two hours for the first 6 hours of the preliminary testing and then again after 24 hours to check for pH fluctuations.

2.3.2 Column Leach Test (CLT)

Columns were used to more realistically simulate field leaching conditions. All specimens were compacted at their 2% dry of optimum moisture contents (OMCs) in an acrylic tube having a 101.6 mm inside diameter and 305 mm height. By compacting to the dry of optimum water content, higher hydraulic conductivities could be achieved that helped allow enough sample to be collected in a reasonable amount of time. Standard Proctor effort (ASTM D 698) was used during compaction. Table 2.4 provides the optimum moisture content and maximum dry unit weights (γ_{dm}) of the mixtures based on compaction tests. The mixtures with the Brandon Shores fly ash were used directly after compaction, However, due to their high calcium content, the mixtures prepared with Columbia fly ash ash were cured for 7 days in a humidity chamber (95% relative humidity, 23 C°) following compaction. Additional information on the column compaction procedures can be found in Appendix B. Figure 2.1 presents a schematic diagram of the column setup. Acid-washed plastic centrifuge tubes were used to store the samples before metal analysis and were labeled using the same system as described above.

After compaction, the column reactors were fabricated by placing porous stones above and below the sample to prevent the compacted media from being washed out of the column and evenly distribute the influent solution. The columns were then capped with top and bottom latex plastic end plates that contained ports for influent and effluent tubing attached to plastic connectors. The plates were held in place using threaded rods, sealed with silicone sealant for a water-tight connection. Influent to the column was provided in a downflow flow direction via a peristaltic

pump (Cole Palmer, Masterflex Model 7518-00) and 1/4 inch Masterflex plastic tubing (Cole Palmer) at a rate of 60 mL/hr as recommended by Gelhar et al. (1992) and Morar et al. (2010). The influent 0.02 M sodium chloride solution was stored in five-gallon buckets, and continuously mixed by magnetic stirrer.

A total of 10 CLTs were performed in two sets. In each test, sampling of the column effluent was conducted 4-5 times a day for the first 3 days to capture the initial fluctuations in metal leachate concentrations. Sampling frequency was then decreased to 3 times a day, followed by twice a day, daily, and once every two days as the testing duration increased. Acid-washed plastic bottles were used to collect between 30 to 50 mL of leachate samples at each sampling time. All samples were analyzed for pH and EC, and then preserved by acidification with trace metal grade HNO_3 to $\text{pH} < 2$ and refrigeration (4°) for later metals analysis. The pH of the influent solution was measured at least twice daily and adjusted using 1 N NaOH to ensure it remained within the designated pH range of 6.5-7. The CLTs were run until the EC and pH values appeared to be approaching equilibrium and at least 25 pore volumes of flow (typically 35-65) had occurred.

A tracer study using bromide as a conservative tracer was conducted at the conclusion of both sets of CLTs to provide a basis for comparison to the metal leachate concentrations. The procedure summarized by Morar et al. (2010) was followed. A stock solution of 1000 mg/L bromide was prepared by dissolving 0.64 grams of NaBr (Sigma Aldrich) into 500 mL of the 0.02 M NaCl solution. The bromide stock solution was diluted with additional 0.02 M NaCl influent solution to prepare 100 and 250 mg/L bromide solutions for the first and second set of columns,

respectively. Three or four samples were taken of column effluent prior to the influent tubing being switched to the bromide solution to create a step input. Sampling of effluent during the tracer study occurred every hour initially then decreased to every two hours, with a total elapsed study time of roughly 30 hours. The samples were then analyzed for bromide concentration as described in Section 2.4.2.

2.3.3 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test was conducted on the 12 soil-fly ash mixtures as outlined in EPA method 1311 (U.S. EPA SW-846), except that the size of the extraction vessel was downsized as described for the WLT (George et al. 2007). Based on the TCLP test, extraction fluid #1, an acetate buffered solution, was used as the leaching solution. Sample preparation, mixing, and post-mixing handling followed the steps described above for the WLT except that the leachate collected after centrifugation was vacuum filtered through TCLP glass fiber filters (Fisher Scientific) instead of membrane filters. Electric conductivity and pH measurements were taken for all samples immediately after filtration. The filtered leachate was then acidified to $\text{pH} < 2$ using trace metal grade HNO_3 and refrigerated until analyzed for metal concentrations.

2.4 Analytical Methods

2.4.1 pH and electrical conductivity (EC) measurements

Measurements of pH were performed using a combination pH probe (Orion, Model 91560) and meter (Orion, Model 520A). The meter was calibrated before each use

using standard buffer solutions at pH 4, 7, and 10. The probe tip was thoroughly rinsed with deionized water between each standard and sample measured.

Calibrations were performed roughly every 4 hours during the CLTs and two hours for the WLTs. A conductance meter (YSI, Model 35) was used to measure electrical conductivity. The tip of the probe was repeatedly submerged a minimum of three times into the solution being tested to allow the EC meter to stabilize. Once the same EC value was measured three times successively, it was recorded. Again, thorough rinsing of the probe was carried out to prevent contamination.

2.4.2 Bromide Measurements

Bromide concentrations were measured using a voltmeter (Orion, Model 520A) equipped with a Br selective membrane probe (Cole Palmer, Model 27506-00), which was used according to the manufacturer's instructions. Five standards (1, 10, 50, 100, and 500 mg/L bromide) were made by serial dilution of the stock solution described in Section 2.3.2. An ionic strength adjuster (ISA), 5 N NaNO₃, was added to both standards and samples in a ratio of 1 mL ISA to 50 mL standard or sample. Standards were thoroughly mixed and a calibration was performed every two hours during the tracer studies, with duplicate measurements. The average voltage values were used to construct a calibration curve relating meter voltage to bromide concentration. Linear regression was performed and only calibration curves with R² values of greater than 0.995 were used to convert sample voltage readings to Br concentration.

2.4.3 Leachate Metal Concentrations

The samples from all of the leaching tests were analyzed for heavy metals using an atomic absorption spectrophotometer (Perkin Elmer, Model 5100ZL) equipped with a graphite tube furnace module. A separate FIAS-400 hydride generator was used to determine concentrations of arsenic. AS-90 and AS-71 autosamplers were used to assist in sample analysis for the furnace and hydride generator apparatuses, respectively. Hollow cathode lamps were used for chromium and copper, while an electrodeless discharge lamp with a Perkin Elmer EDL System 2 power source was required for arsenic. The lamps were set at the following wavelengths specific to the metal being analyzed for: 193.7 nm for As, 357.9 nm for Cr, and 324.8 nm for Cu.

Certified stocks solutions of 1000 mg/L (Fisher Scientific) were used to prepare sets of standards for each metal. Five to six standards were created, ranging from 2 to 40 µg/L for chromium and copper and 0.5 to 10 µg/L for arsenic based on the range where a linear relationship between absorbance and concentration was found. The standards were made using the same background matrix as the samples. Calibration curves with an R^2 value of greater than 0.99 were used. Two standards were measured as samples before and after sample analysis to check the accuracy of calibration and precision of instrument. An approximately 1 mL aliquot of each sample was placed in plastic cups, transferred to the autosampler rack, and analyzed. Estimated metal concentrations in the leachate were calculated from calibration curves produced internally by the AA instrument software. Metal concentrations and sample absorbance values were recorded for each sample duplicate. Dilutions were made when necessary to ensure a sample's absorbance was within the range of

standards used. A new calibration curve was constructed every 20-25 samples. The detection limits of the equipment based on the 0.02 M NaCl leaching solution for As, Cr, and Cu as determined by the EPA Method Detection Limit procedure (Standard Method 1030C) were 0.22, 0.35, and 1.00 µg/L, respectively. Method detection limits were higher for the TCLP Extraction Fluid #1 matrix, and were determined to be 0.49, 1.8, and 1.4 µg/L for As, Cr, and Cu, respectively.

Chapter 3: Results and Discussion

WLT, TCLP, and CLT leaching tests were performed on the same 8 different fly ash-soil mixtures to evaluate the metal leaching behavior as a function of the characteristics of the different testing protocols and the soil/fly ash properties. In addition, pure fly ash and pure soil samples were tested to provide a basis for comparison in terms of expected upper and lower bounds for metal leaching. A series of WLTs were conducted at variable pH values to observe the effect of pH on leaching. Leachate pH and Cu, As, and Cr concentrations were monitored in the three tests and compared to the Maryland State Aquatic Toxicity limits (MDE COMAR) and EPA Drinking Water MCLs (EPA Drinking Water Contaminants). In the following paragraphs, the Cu, As, and Cr concentrations observed in the three tests are discussed sequentially, specifically as a function of the fly ash content and the solution pH. Subsequently, the CLTs are examined in more detail, focusing on the reproducibility of the tests, and interpretation of the tracer study results. Finally, the results of the three test methods are compared.

3.1 Leaching Test Results: Copper

3.1.1 General Trends

Cu concentrations in the WLT leachate (Table 3.1) were below the strict Maryland chronic Cu Aquatic Toxicity limit of 9 $\mu\text{g/L}$ in 75% of the fly ash-soil mixture samples, with the exception of the C-C-10 and C-C-20 samples at 12 and 14 $\mu\text{g/L}$, respectively. These differences in leaching behavior are likely the combined result of the fly ash and soil composition (e.g., metal content and alkalinity) and other factors,

such as pH, which are discussed further below (Bin Shafique et al. 2002, Palumbo et al. 2007). For example, based on the TEA (Table 2.1), soil C (27.16 mg/kg) and C fly ash (188.56 mg/kg) had a higher Cu content compared to soil S (1.28 mg/kg) and the BS fly ash (59.63 mg/kg). Correspondingly, mixtures containing C fly ash generally had higher leachate Cu concentrations (up to 6 times) than similar mixtures with the BS fly ash. The exception to this was the 100% fly ash samples, where both fly ashes had WLT Cu leachate concentrations below 3 µg/L.

The TCLP results (Table 3.2) showed Cu leaching increased in all soil S mixtures compared to the WLT, especially for fly ash BS, while soil C mixtures had TCLP Cu concentrations that were approximately the same as the WLT for the BS fly ash and about 40-50% lower for the C fly ash. TCLP Cu concentrations in the soil C mixtures were all below the Maryland Cu Aquatic Toxicity chronic limit, but three out of the four soil S mixtures (S-C-10, S-BS-10, and S-BS-20) had Cu concentrations exceeding that criterion.

Based on the replicate CLTs for the S-BS mixtures (Figure 3.1), Cu leaching exhibited a first flush behavior, with concentrations decreasing from 12-20 µg/L to < 5 µg/L after the first 1-2 PV. Interestingly, the S-BS column with the higher fly ash content (i.e., 20% vis-à-vis 10%) did not always have the higher Cu concentration in the leachate. The replicate C-BS CLTs also exhibited a first flush behavior (Figure 3.2); however, lower initial peak Cu concentrations (~ 7 µg/L) were measured in the C-BS-20 columns compared to the initial peak Cu concentrations in the S-BS columns (~ 20 µg/L) despite soil C having approximately 21 times the copper content as soil S based on the TEA. One possible explanation for the difference in leaching

between the soils is that adsorption of aqueous Cu onto the mineral surface may have occurred at the pH range of 4-6 for the BS fly ash CLTs and contributed to the reduced leaching found from soil C. For example, in column studies under acidic conditions, Ariese et al. (2002) observed a large portion of the leached metals were retained by the soils, reducing aqueous concentrations by different adsorption or binding mechanisms. Soil C, with a higher percentage of fines (silts and clays), is likely to have increased surface area and surface charge compared to soil S, which are important factors in determining soil adsorption capacity.

Both the S-C-10 and S-C-20 columns had initial Cu concentrations above 20 µg/L (Figure 3.3). These concentrations decreased dramatically with continued leaching, and after 5 PV concentrations were below the Cu Aquatic Toxicity limit. The C-C-20 column exhibited similar leaching behavior as the S-C columns (Figure 3.4). The initial peak Cu concentration was measured at 110 µg/L, or about 12 times the Maryland aquatic toxicity chronic limit for Cu, but concentrations stabilized around 12 µg/L after 20 PV.

CLT leaching of Cu from the soil S-fly ash mixtures was comparable both in behavior and magnitude to that of the 100% soil S column (Figure 3.5). This indicates that the soil can act as a source of metal ions, especially given that 80-90% of the mixture mass is soil and if the soil contains metals in more easily solubilized forms compared to fly ash. The contribution of soil to leaching would vary with its composition and fluctuations in pH. Soils can play a large role in metal leaching because of their effect on processes that govern leaching mechanisms as well as serving as a “compartment” for the storage and/or release of metals. Since soils can

comprise a large portion (greater than 80% by mass) of the total mixture, soil buffering capacity can influence leachate pH which directly affects metal concentrations. Depending on soil properties, soils can be highly adsorptive and remove dissolved metals or release additional metal ions into solution (Bin Shafique et al. 2007). The effect of the fly ash content and pH on Cu leaching are examined further below.

3.1.2 Effect of fly ash content on copper leaching

Increased fly ash content had less effect on the WLT Cu concentrations in the BS fly ash mixtures than the C fly ash mixtures, with aqueous copper for all BS fly ash mixtures measured at $< 5 \mu\text{g/L}$ (Figures 3.6 and 3.7). For the BS fly ash mixtures, the largest increase in Cu concentration was observed going from 10% to 20% fly ash. In comparison, the C fly ash mixtures showed the largest increase ($9.4 \mu\text{g/L}$ for soil C and $6.2 \mu\text{g/L}$ for soil S) in leachate Cu when fly ash content was raised from 0 to 10% as shown in Figures 3.8 and 3.9; however, the Cu concentrations decreased as the fly ash content increased further, from 10% to 20% and/or 100%.

The trends in TCLP Cu concentrations as a function of fly ash content were also different between the BS and C fly ashes. BS fly ash mixtures exhibited a positive, nonlinear relationship between fly ash content and leachate metal concentration, with higher levels of leaching observed in the soil S compared to soil C (Figures 3.10 and 3.11). This difference could be attributed to the larger surface area of soil C due to a higher clay content, which would facilitate adsorption onto soil particles, including iron and aluminum oxide surface deposits (Evans 1989). On the

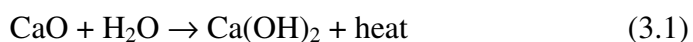
other hand, C fly ash mixtures had a large increase in TCLP leachate Cu concentrations upon the initial addition of fly ash to the soils (from 0 to 10% fly ash by mass), followed by a decrease in Cu concentrations in mixtures with 20 and 100% fly ash (Figures 3.12 and 3.13).

This nonlinear relationship between the leaching of metals from fly ash mixtures with variable fly ash contents has been observed by others (Bin Shafique et al. 2007, Morar et al. 2010) and illustrates the difficulty in predicting leaching behavior. The low metal content in both soils compared to the fly ashes is likely a factor in the nonlinear relationship, especially under the more acidic conditions in the TCLP in which fly ash can serve as the source of the majority of the leached metal. However, as the fly ash content is increased, the percent of soil by mass decreases, thereby reducing the ability of the dissolved metal ions to interact with substances found in the soil. This is particularly relevant to copper because of its high affinity for complexation with humic and fulvic acid portions of soil organic matter, which can cause increased detection of soluble copper (Evans 1989). The difference in TCLP leaching between soils is supported by the higher LOI measured for soil S (8.6%) compared to soil C (7.1%), which would provide more organic matter for Cu complexation.

3.1.3 Effect of pH on copper leaching

Changes in pH can affect the speciation, and therefore the solubility, of metals in the leachate. The distribution of common Cu(II) species as determined by the Visual Minteq chemical equilibrium software is shown in Figure 3.14. In the case of copper,

the Cu^{2+} cation is the dominant species at $\text{pH} < 8$ (Evans 1989). Above this pH, hydroxide precipitation of Cu is expected, which would lead to lower measured aqueous levels. However, the presence of inorganic and organic compounds can cause the formation of soluble complexes that can increase leachate metal concentrations (Rigol et al. 2009). For example, comparing the two fly ashes studied, it is clear the approximate 5 unit difference in leachate pH is a major contributor to the increased WLT Cu leaching seen from the C fly ash (Table 3.1). Calcium in fly ash in the form of calcium oxide reacts with water to form calcium hydroxide,



which dissociates to give 1 mole of Ca^{2+} and two moles of OH^- ,



Thus, the higher calcium content in the C fly ash compared to the BS fly ash (14.43% vis-à-vis 0.22%), and correspondingly higher CaO content, result in more alkalinity and pH values around 11.5 as observed in the unbuffered WLTs and CLTs (Table 3.3). Calcium levels in the fly ash have been reported as a major factor in determining the leachate pH because of relatively high levels of calcium compared to other alkaline elements (Palumbo et al. 2007). Conversely, increased acidity can desorb Cu and release more Cu through the dissolution of minerals, as illustrated by

all 4 TCLP soil S samples having higher leachate Cu than the WLT results for the same mixtures (Table 3.2).

To examine the effect of pH on Cu leaching more closely, all batch Cu data were compiled in Figure 3.15 for the S-C mixtures and Figure 3.16 for the C-C mixtures. No clear trends in Cu leaching were observed in the buffered WLTs from the BS fly ash mixtures due to the large scatter of data, so those data are not shown. For the mixtures with C fly ash (Figures 3.15 and 3.16), the Cu concentrations were higher in the samples buffered at pH 7 and 9 compared to those from the original WLTs (pH ~11.5) and the TCLP tests. Similar results were seen for both soils and supported increased leaching of Cu as the pH is decreased from the unbuffered value. This is possibly attributed to higher levels of Cu release from increased dissolution of fly ash and soil particles under acidic conditions and complexation reactions with positively-charged Cu species and negatively-charged soil organic matter resulting in higher soluble Cu levels (Fytianos et al. 1998, Ram et al. 2007).

The pH also impacted the results of the CLTs. The BS fly ash columns exhibited more fluctuations in the CLT pH measurements, sometimes changing 1-2 pH units within several pore volumes. In contrast, columns containing C fly ash had stable pH measurements throughout the test duration. There were certain CLTs, such as the S-BS-20 (Figure 3.1) and C-BS-20 (Figure 3.2) columns, where in some portions of the leaching curves there appears to be a correlation between decreases in pH and increased Cu concentrations. This confirms the importance of pH in determining leachate metal concentrations, and how simple pH measurements can aid in predicting metal speciation and leaching behavior.

3.2 Leaching Test Results: Arsenic

3.2.1 General Trends

Aqueous WLT arsenic concentrations were measured below the EPA MCL of 10 µg/L for all fly ash-soil mixtures (Table 3.1). In fact, leachate As concentrations were generally < 1 µg/L with little variation between mixtures of different soils or fly ashes in the WLTs, except for the 100% BS fly ash at 23 µg/L. This suggests that the same leaching mechanisms are occurring in mixtures of the different soil and fly ashes. The low (generally < 1 µg/L) levels of As detected also suggest that soluble arsenic is either being strongly adsorbed or precipitated out of solution.

Similarly, the aqueous TCLP arsenic concentrations were also measured at below the EPA MCL for all soil-fly ash mixtures (Table 3.2). However, both 100% fly ash samples exceeded the MCL with concentrations of 30 and 85 µg/L for C and BS fly ashes, respectively. The TEA results (Table 2.1) indicate that the arsenic content of the BS fly ash is higher than that of the C fly ash (24.2 mg/kg versus 15.0 mg/kg), consistent with the higher leaching in the 100% BS fly ash samples. The S-BS-20 mixture had the highest TCLP As concentration of the soil-fly ash mixtures, but the arsenic leachate concentrations for all fly ash-soil mixtures exhibited a very tight range compared to the other metals, with all ranging from < 0.49 to 3.0 µg/L. Thus, the presence of the soils dramatically influenced the As concentrations in the leachate. The addition of fly ash to soil C appeared to have a less pronounced effect on As leaching as the 100% C soil samples had a slightly greater concentration for leachate arsenic (1.7 µg/L) than the fly ash-soil mixtures (<0.49 to 1.1 µg/L).

Peak leachate As concentrations did not exceed 40% of the EPA MCL for any of the CLT specimens, but the patterns varied depending on the soil and fly ash properties. S-BS As leaching in the CLTs followed first flush behavior with a maximum initial concentration around 3 $\mu\text{g/L}$ (Figure 3.17). Arsenic leaching was higher in the S-BS-20 mixture, illustrating that increasing the fly ash content can result in larger leachate concentrations under some conditions. A very different pattern was observed for the As concentrations in the S-C-10 and S-C-20 columns, in which case As increased with time, albeit still remaining below the EPA MCL (Figure 3.18). Further testing is needed to better characterize leaching in relation to regulatory limits under a longer leaching period. Arsenic can become more solubilized under alkaline conditions, such as observed in the S-C mixtures, and leach in greater quantities because of electrostatic repulsion between anionic As species and negatively-charged soil particles (Palumbo et al. 2007, Jegadeesan et al. 2008). As concentrations in the C-C-20 column also remained below the EPA MCL throughout the test duration, but showed a slight increase to approximately 2.0 $\mu\text{g/L}$ (Figure 3.4). Leaching of arsenic in the C-BS-20 columns (Figure 3.19) peaked after several PV and then rapidly decreased. The generally low levels of As leaching ($< 5 \mu\text{g/L}$) could be the result of the strong attraction of As species to soil particles (increased adsorption of dissolved As) and possible precipitation of As as some type of iron-lead oxide. High levels of As retention by soils were found in both highly organic and highly mineral soils, which may have contributed to lower aqueous levels detected (Balasoiu et al. 2001).

3.2.2 Effect of fly ash on arsenic leaching

BS fly ash mixtures generally had increasing WLT As concentrations as the fly ash content was raised from 0 to 100% fly ash (Figures 3.6-3.7) , although the relationship was nonlinear. The soil C mixture actually had a small decrease in As concentrations increasing from 10 to 20% fly ash content, but the increase from 20 to 100% fly ash produced the largest increase in concentration up to 22 µg/L. This fly ash content increment corresponded to the largest change in leachate WLT pH (2.8 pH unit increase for S-BS and 2.2 pH unit increase for C-BS) (Table 3.1), supporting the connection between changes in pH from fly ash addition and the amount of leached metalloid or metal, as discussed further below. The C fly ash mixtures for both soils showed an increase in WLT As concentration from 0 to 10% but decreased as the fly ash content was raised further (Figures 3.8-3.9). This initial increase in As concentration also corresponded to the largest pH change in the WLT samples, an increase of 5.8 units for soil S mixtures and 2.6 units for soil C mixtures. Higher leaching from the 100% BS fly ash compared to 100% C fly ash (Table 3.1) is likely to be related to the higher As content of this fly ash by roughly 10 mg/kg based on the TEA (Table 2.1).

In the TCLP test, increasing the fly ash content from 10 to 20% resulted in 1-2 µg/L higher As concentration in the leachate for soil S samples with both fly ashes (Figures 3.10 and 3.12), but this trend was not seen with soil C (Figures 3.11 and 3.13). The largest increase in As concentration in all of the TCLP tests occurred with the increase from the 20 to 100% fly ash content, and could be the result of the

absence of soil particles that enhance adsorption or release precipitating agents from the fly ash which such as lead or sulfide.

3.2.3 Effect of pH on arsenic leaching

Previous studies have found that As is found in fly ash primarily as As(V), possibly due to the highly oxidizing environment of coal combustion, which would convert arsenite (As(III)) species to As(V) species (Cullen and Reimer 1989, Shah et al. 2008). A distribution of As(V) species produced by Visual Minteq software is provided in Figure 3.20. Alkaline pH conditions favor increasingly negatively-charged As species, such as HAsO_4^{2-} and AsO_4^{3-} for As(V), to dominate in solution, with the latter present in appreciable quantities at $\text{pH} > 11$. However, if As(III) is the main form of As present in the fly ash, then leaching could produce arsenous acid (H_3AsO_3) or H_2AsO_3^- . Arsenite can become more significant at higher pH values and in reducing environments, such as may have occurred in the closed, saturated CLT system. This is important because retention of As(III) by soils is less than that of As(V) (Balasoiu et al. 2001). If dissolved concentrations exceed the adsorption capacity of the soil, increased leaching of arsenic can be observed because of repulsion between the metal ion and the soil particle surface. Therefore, at very alkaline pH values above 11, As species can exhibit reduced adsorption to negatively-charge surfaces and therefore leach in higher concentrations under conditions such as those seen with the C fly ash (Wang et al. 2006, Morar et al. 2010). A more in-depth speciation study would be helpful in confirming the As species present and providing evidence of the observed leaching behavior.

Consistent with the discussion above, the S-BS mixtures showed relatively constant As levels from pH 5-7, but increasing As concentrations in the batch leach tests as the pH rose from 7 to 9 (Figure 3.21) , although this was not clearly observed in the C-BS samples (data not shown). In the latter case, the finer particles of soil C may have promoted more adsorption via the increased surface area of iron and manganese oxides. In contrast, arsenic leaching for C fly ash mixtures with soil S increased from pH 5 to 7-9, then decreased with an additional pH increase to 11 (Figure 3.22) except for C-C-10 which had a slight increase (data not shown). The large, roughly 5 unit difference in pH is likely a major factor in the different observed leaching results. The different As species dominant at the slightly acidic pH (BS fly ash mixtures) and basic pH (C fly ash mixtures) would have different adsorption, complexation, and precipitation capacities. At TCLP As leaching from both fly ashes mixtures all had concentrations < 3 µg/L, reflecting the similar pH conditions.

3.3 Leaching Test Results: Chromium

3.3.1 General Trends

Except for the 100 µg/L of aqueous Cr measured in the C-C-20 mixture, all other WLT Cr levels were below the 100 µg/L EPA MCL (Table 3.1). WLT Cr concentrations ranged from 57-100 µg/L for C fly ash mixtures compared to <0.35 to 1.4 µg/L for BS mixtures. Thus, Cr leached from S-C mixtures at concentrations ranging from 160-190 times the concentration for the corresponding S-BS mixture, and C-C mixtures at concentrations approximately 50-80 times more than from the corresponding C-BS mixture. All of the C fly ash samples with elevated Cr levels

had pH values > 10, similar to the results obtained by Fytianos et al. (1998) and Palumbo et al. (2007).

TCLP Cr concentrations were measured below the EPA MCL for Cr in all soil-fly ash mixtures (Table 3.2). Only the 100% C fly ash exceeded the MCL, consistent with the relatively high Cr content of this fly ash based on the TEA (64.6 mg/kg). With the exception of the S-C and C-C mixtures, all of the TCLP Cr concentrations exceeded the WLT Cr concentrations. This is probably due at least in part to the lower pH of the TCLP (average pH of 6.3 for 100% C fly ash samples). Zandi and Russell (2007) describe how certain metals such as Cr are typically found in the glassy, exterior coating of the fly ash particles resulting from condensation following coal combustion. More acidic conditions degrade this surface Cr and release it into solution, leading to more dissolved Cr as seen in the BS fly ash mixtures. In addition, the lower pH range (4.8 to 6.3) of the TCLP favors the dominance of cationic species of Cr such as CrOH^{2+} and $\text{Cr}(\text{OH})_2^+$ that would adsorb less to soils under acidic conditions because of the dominance of positively-charged surfaces.

Several of the CLT tests exhibited a lagged leaching response for Cr, and had portions of the leaching curves that showed decreases in pH resulting in increased Cr concentrations. For example, Cr concentrations from the first set of CLTs with S-BS (Figure 3.23) had the most variation and showed a lagged leaching response with two periods of elevated chromium levels above 50 $\mu\text{g/L}$. A lagged Cr leaching response could be caused by Cr being located in less easily solubilized fractions of the soil and fly ash particles. Thus, as time progresses, leaching solution is able to reach these Cr

sources and dissolution reactions reach the point where the Cr is released into solution. Edil et al. (1992) also observed that while the majority of CLTs exhibited first flush leaching, Cr had a different leaching response. A sharp spike in Cr to 250 µg/L in the first set S-BS-20 column around 10 PV was the only time the CLT leachate concentrations exceeded the Cr MCL limit. Similar lagged spikes in Cr concentration to 35 µg/L and 20 µg/L were observed in the second set S-BS-20 column (Figure 3.23), and first C-BS-20 column (Figure 3.24), respectively, which corresponded to the first major drop in pH. In contrast, both the S-C-10 and S-C-20 columns had initial Cr concentrations that exceeded the EPA MCL (Figure 3.25), but quickly dropped within 5 PV to below regulatory limits. The C-C-20 column also had initial Cr concentrations (238 µg/L) over two times the 100 µg/L regulation limit (Figure 3.4), similar in order of magnitude to leaching from other columns containing C fly ash, followed by declining Cr levels.

3.3.2 Effect of fly ash content on chromium leaching

Fly ash content appeared to have minimal effect on WLT Cr leachate concentrations in the BS fly ash mixtures, with a range of Cr concentration of < 0.35 to 2.8 µg/L in the 100% BS fly ash sample (Figures 3.6-3.7). Mixtures of both soils and C fly ash show an increase in WLT Cr concentration initially with a peak at 20% fly ash before decreasing with 100% fly ash sample (Figure 3.8-3.9). The higher leachate Cr from soil-fly ash mixtures is possibly due to the increased repulsion of Cr species with charged surfaces more abundant in the presence of the soil particles. The presence of soluble soil organic matter could also play an important role in causing increased Cr

in the leachate. Mixtures of fly ash with soil C displayed higher Cr concentrations than the corresponding mixtures with soil S, which may be partially due to this soil having the highest levels of Cr present (65.9 mg/kg) of all 4 materials, although soil C itself had lower leachate levels than soil S (Table 2.1). The relatively sharp increase in metal concentration from 0 to 10% C fly ash can be attributed to the pH change of approximately 6 for soil S and 3 for soil C that occurred from the increase of 0 to 10% fly ash, which may have led to an increased attack on the mineral structure of the soils and dissolution of the exterior coating on fly ash particles.

The TCLP leaching results indicated an approximately linear relationship between leachate Cr concentrations and fly ash content for all soil and fly ash mixtures (Figures 3.10-3.13), with a minimum coefficient of determination determined to be 0.9655 (trendlines not shown). The slope of this relationship is similar for the BS fly ash mixtures, as it is for the C fly ash mixtures, suggesting that the fly ash metal content was determining the results. The more uniform leaching pattern observed corresponds to the more consistent pH in the TCLP samples compared to those from the WLT. The smaller fluctuations in pH with varying fly ash content seen in the TCLP (Table 3.2) could produce a more consistent release of Cr into solution as the acidity with different fly ash contents remains relatively constant.

3.3.3 Effect of pH on chromium leaching

Cr can be present in fly ash as Cr(VI) in low percentages (< 5%) that vary with the coal source and combustion conditions (Shah et al. 2008). The dominance of either the Cr(III) or Cr(VI) form is strongly linked to pH and other conditions such as the pE

of the system, which indicates the thermodynamic driving force for reduction and oxidation of Cr species. Cr(III) typically forms increasingly negative species with minimum solubility around pH 6-7, and eventually precipitates out as $\text{Cr}(\text{OH})_3$ (Rai et al. 1987). At very alkaline pH values greater than 10, Cr(III) can form species like $\text{Cr}(\text{OH})_4^-$, which behaves like other anions with decreased adsorption under alkaline conditions (Shah et al. 2008). This change in Cr(III) speciation is shown in Figure 3.26 which has the relative distribution of Cr(III) species as a function of pH. This anionic behavior is probably a main contributor to the higher unbuffered WLT Cr concentrations from the C fly ash mixtures, which have higher pH values of roughly 11.5 compared to around 6.5 for BS fly ash mixtures (Table 3.3, Figures 3.27-3.28). TCLP Cr concentrations were higher than for the unbuffered WLT as the pH was decreased for the BS fly ash, but the opposite effect was observed for the C fly ash mixtures. The leaching of Cr is generally magnified at acidic pH values compared to negligible leaching occurring in neutral or alkaline conditions as the acidic conditions aggressively attack the Cr-containing compounds in the materials, releasing Cr into solution (Fytianos et al. 1998, Jo et al. 2008). These findings are consistent with the increased leaching of Cr under acidic TCLP conditions observed in the current study for the BS fly ash mixtures.

Consistent with the discussion above, the Cr concentrations in the buffered WLT with the BS fly ash mixtures increased from pH 7 to pH 9, with a similar but less dramatic effect in the C fly ash samples (see Figure 3.27-3.28). The weaker trend with the C fly ash can be explained if a majority of the Cr present in this fly ash was Cr(VI), which has high solubilities over a pH range of 2-12 and, thus, aqueous

concentrations would be similar at different pHs (Rai et al. 1989). A single colorimetric determination of Cr(VI) with diphenylcarbazide reagent performed on one set of CLT samples showed levels of Cr(VI) in the BS fly ash column leachate to be below 1.0 µg/L, while C fly ash had 114 µg/L, which represented approximately 50% of the total leached Cr. Thus, if the BS fly ash mixtures have predominantly Cr(III), then the combined TCLP and buffered WLT test results from this study agree well with the expected bowl-shaped solubility of Cr(III) across the pH scale: at acidic pH values (~ 5.5 for TCLP), solubility of Cr(III) is raised and higher leachate concentrations are observed; similarly, at alkaline pH values (9 for buffered WLT), solubility and therefore leaching of Cr(III) is again enhanced after reaching a minimal around neutral pH (Rai et al. 1987). In comparison, the relatively consistent magnitude of the Cr concentration in the leachate from the C fly ash mixtures across the pH values tested is consistent with Cr(VI) being dominant in C fly ash, whose distribution of species as a function of pH is shown in Figure 3.29. Interestingly, at the high pH values (> 10) where increased leaching of As was found, Balasoïu et al. (2001) found that the presence of arsenate significantly decreased Cr(VI) adsorption on an iron oxide surface deposits due to competition for adsorption sites and electrostatic effects. This potential for interactions between metal ions illustrates another aspect of the complexity of natural leaching mechanisms, especially when dealing with several metals of interest at once.

3.4 CLT Reproducibility

The duplicate columns prepared with soil C and fly ash BS at 20% all exhibited a similar leaching behavior for all of the metals, which could be described as a first flush response pattern (Figures 3.2, 3.19, and 3.24). In addition, with the exception of a spike in Cr concentration in the C-BS-20 #1 column, the magnitude of the leachate concentrations also exhibited good reproducibility, with effluent concentrations that differed by less than 3 µg/L throughout the test. The highly variable pH in the BS fly ash mixtures could explain the difference in leaching behavior in the duplicated columns because sudden fluctuations in pH could affect the solubilization processes occurring in a specific portion of the column.

Duplicate S-BS-10 and S-BS-20 columns showed similar first flush leaching behavior for Cu and As (Figures 3.1, 3.17, and 3.23). Differences in leachate concentration between duplicate CLTs were small at < 5 µg/L for Cu and < 1 µg/L for As throughout the test duration. Cr leached from the S-BS column exhibiting first a lagged and then a first flush leaching response, with the lagged response CLTs have higher measured leachate Cr. Again, differences in the flow through the column media and natural heterogeneity could be the cause of discrepancies in leaching from columns composed using the same mixture.

In addition to pH, another factor that could contribute to variability between replicate columns is the formation of preferential flow paths, which could facilitate the solubilization of portions of the column having varying amounts of metals present. This is supported by the difference in breakthrough times between the first and second set of CLTs. In addition, due to the heterogeneous nature of the soils and

fly ash, differences within materials could contribute to fluctuations in both metal concentration and effluent pH. Nonetheless, although differences exist in leaching between columns composed of the same mixture, the results show that CLTs can be reproduced and similar estimates of leaching potential obtained.

3.5 Tracer Study Results

Bromide breakthrough curves showing C/C_0 as function of pore volumes of flow for both sets of CLTs are shown in Figures 3.30-3.31. All of the tests were performed in the same manner, although there was less variation in influent solution bromide measurements from the second set of CLTs. Breakthrough curves are useful tools in assessing the transport parameters of mixtures and evaluating the presence of flow anomalies such as preferential flow paths that could impact the leaching of heavy metals as the leaching solution flows through the column media. Despite some inconsistency in the influent bromide concentrations, the breakthrough curves for all 10 columns were similar, with all exhibiting the typical “S” curve response to the step input of bromide. However, there was some variability in the timing of the breakthrough point, which was reported as reached when the C/C_0 ratio approximately equaled 1. For example, the tracer studies for the first set of CLTs (Figure 3.30) had earlier breakthrough points compared to the second set of columns (Figure 3.31). In addition, within the first set, the type of fly ash appeared to have a strong impact on the point of breakthrough, with the C fly ash mixtures having breakthrough occur earlier than the BS fly ash mixtures, at approximately 0.25 and 0.75 PV, respectively. In comparison, all columns from the second set of CLTs had

breakthroughs occur at roughly the same time around 1 PV as expected for a conservative tracer.

One possible explanation for the observation of an earlier breakthrough in the first set of C fly ash columns compared to other columns could be the increased porosity that results from combining the soils with a smaller particle size fly ash. However, this phenomenon should have affected the BS fly ash columns as well. Therefore, it is more likely that these results suggest that there was either short circuiting along the column walls or preferential flow paths could have developed within the fly ash columns that would allow leaching solution to pass through the columns more rapidly than expected, thereby changing the extraction time and metal leaching behavior.

3.6 Comparison of Different Leaching Test Results

There were significant differences in the leachate metal concentrations obtained in the three leaching tests performed, as shown in Table 3.4 and Figures 3.32-3.34. When comparing results from leaching test methodologies, it is important to consider the impact of chemical factors, such as pH differences, and hydrologic conditions (flow-through or static). For example, critics of the use of the TCLP for evaluating the leaching potential of fly ash point out that the more acidic test conditions characteristic of landfill leachate often result in higher leaching and can overestimate the leaching potential of fly ash mixtures when placed in other environments (Baba and Kaya 2004). This is demonstrated by the results of a study by Jegadeesan et al. (2008) comparing the synthetic precipitation leaching procedure (SPLP), which uses

a sulfuric and nitric acid mixture as the leaching solution for fly ash, and the TCLP test. They found that aqueous As and Cr concentrations were three times higher in the TCLP tests, while Cu concentrations were <0.006 mg/L for the SPLP compared to 0.81 mg/L for the TCLP (Jegadeesan et al. 2008).

In comparing the batch results from this research, pH was the major factor contributing to the different observed metal leachate concentrations. Leachate concentrations from the TCLP were generally higher compared to those from the WLT for both Cu and As (Figures 3.35 and 3.36), with the exception of C-BS-10 and five of the C fly ash mixtures, for which the WLT concentrations were higher. Increased Cr concentrations were also seen in the WLTs for all of the C fly ash mixtures (Figure 3.37). TCLP As concentrations were higher than the WLT results for the 100% fly ash samples by approximately 30 $\mu\text{g/L}$ for C fly ash and 60 $\mu\text{g/L}$ for the BS fly ash (Tables 3.1 and 3.2). In comparison, the increases in the TCLP As concentration observed in BS fly ash mixtures were small (< 2 $\mu\text{g/L}$) compared to the WLT results. Jo et al. (2008) also reported leaching of As and Cu concentrations similar in magnitude from bottom and lagoon coal ash. The magnitude of the difference in pH between the TCLP (~ 5.3) and WLT (~ 6.5 for BS fly ash and ~ 11.5 for C fly ash) is largely responsible for explaining the different leaching trends. The difference between the TCLP and WLT concentrations were lower for the BS fly ash mixtures because of the smaller differences in pH (~ 1 pH unit) compared to the C fly ash mixtures (~ 7 pH units) which had Cr concentrations roughly double from the TCLP to the WLT.

When comparing the batch and CLT results, both pH and contact time become important. In this regard, the work by Ariese et al. (2002) is helpful in explaining some of the findings in this study. Ariese et al. (2002) concluded from pH-stat experiments on several different fly ashes at pH 3 and 5 that extraction time (7 vis-à-vis 24 hrs) had little effect on leachate concentrations, indicating equilibrium was possibly reached early on. This observation is consistent with the first flush leaching behavior seen in the majority of the CLT results, with highest transformation and transport of metal ions occurring in the beginning of the leaching test. Furthermore, sequential extraction tests performed by Ariese et al. (2002) showed that the readily exchangeable fractions of Cu comprised 60% of the total extractable amount. Thus, the high Cu concentrations leaching from the C fly ash in some of the CLTs in this study could result from increased solubilization from cation exchange reactions and steady-state being achieved early on. Ariese et al. (2002) also found that leachate Cu concentrations were higher under more acidic conditions. This confirms that changing the testing conditions, including lowering the pH, can affect metal leachate concentrations and yield higher or lower estimates of leaching potential. For example, elevated levels of Cr were measured at alkaline pHs in this study, and leachate Cu and Cr concentrations at pH 5 from the same pH-state tests by Ariese et al. (2002) were similar to the TCLP results from the current study. The different leaching behavior seen for the three metals studied reflect their different speciation and adsorption/precipitation mechanisms.

Performing a reasonable comparison of the batch leach tests to the CLTs also requires careful consideration of the point of comparison. For this work, two

different comparisons were made. First, the peak column effluent concentrations were determined, which correspond typically to the initial first flush or concentrations measured with the first or second PV. Caution should be used, however, when comparing peak values as sole spikes in metal concentration could misrepresent the overall leaching behavior of the column. Second, a volume-weighted mean concentration (MC) was calculated using the highest L:S ratio common to all 10 columns. Calculated L:S ratios for the columns ranged from 4.8 and 5.1 because of differences in the sampling schedules between columns. The target L:S ratio was 5, which corresponds approximately to 25 years of leaching conditions (Ram et al. 2007) assuming typical dilution factors from normal groundwater flow. By examining the temporal change in leachate metal concentrations over longer time periods (weeks to months), CLTs allow estimations of leaching to be made that reflect both conditions more similar to the field and time frames that simulate prolonged leaching from a highway embankment with dozens of PV passing through the column representing many sequential rain events that could cause metal leaching.

Previous studies (Bin Shafique et al. 2007, Ram et al. 2007) report that peak leachate metal concentrations were higher in the CLT compared to WLT as was observed in the current study (Figures 3.32-3.34). Peak Cu, Cr and As CLT concentrations were higher than those from the WLT for all sample mixtures, except S-BS-10 and C-C-10. The peak Cu, Cr, and As CLT concentrations were also higher than the TCLP except for Cu in the S-BS-10, C-BS-10, and C-C-10 mixtures, As in the S-BS-10, C-BS-10, and C-C-10 mixtures, and Cr for the C-BS-10 mixture. Again this was possibly due to the increased acidity and favorable conditions for dissolution

in the TCLP. The higher fixed L:S ratios (20:1 in the TCLP and WLT) found in batch leach tests can explain the lower concentrations generally found in the leachate of those tests. High initial concentrations of metals are also commonly found in the first few PV from CLTs because of the lower L:S ratio at the beginning of the CLT. However, as the saturation increases, the L:S ratio increases and concentrations generally decrease (Jo et al. 2008). Thus, the CLT MC concentrations are generally reduced for all metals compared to the peak concentrations, as expected given the typical exponential decrease in leaching observed in CLTs. Based on these results, it is expected that both test duration and L:S ratio are important parameters in comparing the results of CLTs and batch tests, while the pH of the TCLP distinguishes its leaching results from other testing methods.

Work done by Bin Shafique et al. (2006) and Ram et al. (2007) compared WLT and CLT results to estimate conservative scaling factors (e.g., 10 for Cr) for converting estimations of leachate metal concentration between WLT and CLT. Relative leaching of the three tests performed in this research was consistent with these other studies comparing different leaching protocols, with the fly ash and soil composition accounting for any differences. From this work, the ratio of CLT peak concentration to WLT concentration ranged from 3.1-5.5 for As, 1.9-12.4 for Cu, and 2.4-714 for Cr. These ratios, however, are noticeably reduced when the CLT mean concentrations are used: 0.9-2.5 for As, 0.3-1.9 for Cu, and 0.5-60 for Cr (see Table 3.5). Figures 3.32-3.34 show that in the C fly ash and BS fly ash mixtures, the peak CLT concentrations were 2-8 and 1-15 times the highest TCLP or WLT leachate metal concentration, respectively. Clearly, the batch tests confirm the importance of

pH in metal leaching and the CLTs show how much leachate metal concentrations can vary with time.

Table 3.6 provides estimations of leachate metal concentrations for a theoretical 100% leaching scenario, where all metal present in the soil-fly ash mixture is solubilized and released into the leachate. Though very unlikely to happen in the field, the leaching predictions provide a useful frame of reference. For example, the highest predicted As concentration for 100% leaching is 9.87 mg/kg, which is orders of magnitude greater than the highest concentrations reported from the leach tests. A comparison between Table 3.4 and Tables 3.6 indicate that even the highest leaching observed is resulting from only a small portion (<10%) of the total metal present in the mixture becoming dissolved in solution.

The effect of extraction time and solution pH are connected to the distribution of metals in different fractions, such as exchangeable, attached to Fe oxides, or contained in carbonate compounds. Ram et al. (2007) describe two phases or “compartments” where metals can accumulate within the materials: the magnetic (Cu) phase and the non-magnetic (Cr and As) phase, which primarily involves the fly ash particle surfaces with high dissolution capacity and is similar between both batch and column leach tests. For example, Cr leaching was shown by Zandi and Russell (2007) to be controlled by the amount of the metal present in the fly ash; therefore, estimations of aqueous Cr could be made from knowledge of concentrations of metals in the soils and fly ashes. This agrees with the near linear relationship between fly ash content and leachate concentration in the TCLP tests of this study. As stated before, the properties of the materials used in fly ash-soil mixtures can have a major

effect on the processes that contribute to overall leaching behavior, such as precipitation, sorption, and dissolution. Wang et al. (2004) states that surface characteristics such as surface charge, specific surface area, and metal binding capacities govern the metal partitioning in fly ash. While some of these properties (e.g., effective surface area) have been extensively studied, others such as metal binding site densities and acidity constants have not been quantified. Continued research into examining these mechanisms and properties would be useful, especially in the development and verification of leaching models.

Chapter 4: Practical Implications

Obviously two of the most important parameters to consider when selecting a protocol for assessing metal leaching from fly ash are pH and the L:S ratio. While sorption processes play an integral role in determining metal concentrations in the leachate, large fluctuations in pH can facilitate the dissolution of metal-containing minerals, especially under acidic conditions (Bin Shafique et al. 2007). Changes in pH over time affect the amount of metals released into solution, but also what precipitates and complexes are formed that affect the re-adsorption of dissolved metals and mobility of metals in the environment. In this study, the pH measurements in the WLTs and CLTs exhibited a larger pH range than in the TCLP that more clearly illustrates the effect of fly ash composition on leachate pH. A comparison of leaching protocols provided by this study highlights the importance of pH, as well as leaching time and the L:S ratio, for understanding the larger picture for a given fly ash mixture.

The higher L:S ratios seen in batch tests compared to CLTs can be viewed as representative of more dilute leaching, possibly related to potential groundwater contamination, while CLTs can simulate leaching behavior seen in the soil solution in areas immediately close to the fly ash-soil mixtures. Thus, different leaching tests can represent different scenarios, including the soil solution in the areas containing the fly ash-soil mixture or estimations of concentrations of metals that might migrate to groundwater supplies. For example, initial results from CLTs would likely overestimate risk of leaching if regulations compare leachate concentrations to federal drinking water standards (Jo et al. 2008).

While CLTs can provide more realistic leaching measurements given the more site-specific and flow-through conditions, WLTs, on the other hand, are viewed as a rapid method to gain reasonable estimation of metal leaching concentrations. Batch leach tests require less time to run and a simpler experimental setup, which is why they are typically included in regulations governing CCB disposal. These tests, however, can misrepresent actual field conditions by having pH values or L:S ratios not typically seen in the field. For example, the increased metal leaching found under TCLP conditions observed for some metals and fly ash mixtures in this study supports the statement that the TCLP leaching solution is too aggressive, while tests like the ASTM WLT provide more a reasonable simulation of natural leaching conditions (Baba and Kaya 2004). The WLT or CLT is preferred because their leaching solution is more similar to the natural water that would flow through an embankment compared to the acetic acid solution used in the TCLP to simulate landfill leachate conditions. Additionally, the hazardous waste criteria pertaining to heavy metal concentrations listed in the TCLP standard procedure are much less stringent compared to the Aquatic Toxicity limits or the EPA MCLs (mg/L vis-à-vis µg/L). For this reason, the listed concentrations do not accurately reflect the hazards to environmental or human health.

Furthermore, the flow-through nature of CLTs compared to the static, contained system in the TCLP and WLT provides different contact times, soil-fly ash interactions, and L:S ratios that can alter the reactions and equilibration processes which affect final pH and aqueous metal concentrations. Clearly, leaching in an actual highway embankment is more accurately characterized by the downward

infiltration of rain or movement of surface runoff than the end-over-end tumbling action used in the batch tests. Ram et al. (2007) states that column tests are preferred to evaluate long-term leaching and risks to the environment/humans, but batch tests should also be incorporated into guidelines. CLTs can be more easily adjusted to fit certain site-specific conditions, including changes to the influent flow rate and the physical properties of the fly ash medium such as unit weight, moisture content, and porosity. This would allow for leaching results to be obtained that better reflect environmental conditions in a certain area, and more accurately assess potential risks and alternatives for CCB disposal.

Based on the results of this study and the work of others (Baba and Kaya 2004, Bin Shafique et al. 2007, Zandi and Russell 2007), a leaching test protocol was developed, which combined batch and column tests aimed at characterizing different aspects of leaching behavior (Figure 4.1). The proposed protocol includes preliminary work aimed at characterizing the materials and using knowledge of field conditions to select the test parameters. Preliminary batch leaching tests can serve as an integral part of the testing framework to provide initial fly ash mixture characterization and pinpoint reasonable parameters for future testing. In the first step of the proposed protocol, the application scenario of interest is defined, and the pertaining regulatory constraints assembled. In addition, the fly ashes and soils are characterized in terms of their pH, total elemental analysis, and geotechnical properties. Then batch WLTs are performed with the soil-fly ash mixtures of interest to determine the system parameters, such as pH, and their effect on metal leaching.

Batch tests are used initially because they are advantageous when a large number of fly ashes mixtures are being screened for use in actual construction. Next, candidate fly ash-soil mixtures that result in increased leaching based on the WLTs are selected and subjected to CLTs to evaluate the spatial and temporal evolution of key system parameters and metal concentrations. CLTs would provide a more detailed evaluation of long-term leaching potential for the selected mixtures. By comparing the WLT and CLT leachate metal concentrations to applicable state and federal water quality criteria, risks from heavy metal leaching could be gauged. The goal of the proposed protocol is provide a flexible testing framework that attempts to most closely simulate field leaching conditions while allowing evaluation of fly ash mixtures under varying detail, cost, and time constraints. When a simpler approach is needed (there is neither the time nor resources to run CLTs), the quicker WLTs could be used and additional factors such as the L:S adjusted to be more consistent with field conditions.

It is important that the protocols developed for the testing of CCBs be sufficiently flexible that a variety of leaching conditions can be investigated in one study, including area-specific factors. The testing of fly ash and other CCBs should incorporate standardized leaching tests that provide regulators and other interested parties with a mechanism for encouraging CCB reuse and the development of disposal guidelines. Continued research in characterizing the leaching of fly ash-soil mixtures is needed to better understand the leaching behavior of these materials and the different factors that affect it. Selecting a leaching protocol that provides both consistent and realistic predictions of metal leaching has ramifications in both the

protection of natural ecosystems and the costs and time required for proper fly ash waste management and disposal.

Chapter 5: Summary and Conclusions

Three different leaching tests (WLT, CLT, TCLP) were performed on fly ashes, soils, and fly ash-soil mixtures to evaluate the As, Cu, and Cr leaching behavior of these materials and provide a comparison between the leaching test methodologies.

Leachate metal concentrations were compared to federal and state regulatory water limits to evaluate the potential risks from heavy metal leaching. Consistent with similar leaching studies, key factors considered when comparing the relative leaching with the different tests, and the leaching behavior of the three metals, were the solution pH and the following testing parameters: leaching solution composition, L:S ratio, and extraction time.

The large difference in leachate pH values between the BS and C fly ashes led to noticeable effects in the leachate metal concentrations. C fly ash-soil mixtures showed higher levels of leaching for all metals in the WLT than the corresponding BS fly ash mixtures, consistent with the more alkaline conditions created by this fly ash compared to the BS fly ash. For example, the repulsion between anionic metal species and the negatively-charged soil surfaces at pH values > 10 probably contributed to the increased leaching seen with fly ash C. In addition, complexation with soluble organic matter is also a contributing factor to leaching, particularly for Cu, which is usually precipitated out at high pHs. Nevertheless, in 75% of fly ash-soil mixtures tested, none of the regulatory limits were exceeded by WLT leachate metal concentrations, as shown in Table 3.1.

TCLP leaching results between fly ashes were mixed, with more As and Cu leached from the S-BS mixtures compared to the S-C mixtures, and more Cu leached

from the C-C mixtures than the C-BS mixtures, but with similar As levels. Elevated Cr concentrations were measured for the C fly ash mixtures compared to the BS fly ash mixtures. TCLP metal concentrations were observed to be higher than those from WLTs in the majority (about 60%) of mixtures. Leaching of Cr from the C fly ash mixtures was one of the exceptions to this trend, where WLT Cr concentrations were approximately two to three times the TCLP concentrations. Leaching of the 100% fly ashes was also magnified under TCLP conditions compared to those found in the WLT, with the exception of Cu for the C fly ash, consistent with increased dissolution of minerals and solubilization of metals at low pHs.

The results of the CLT showed that the fly ash-soil mixtures typically exhibited one of two different leaching behaviors as described by Edil et al. (1992): first flush or lagged response. Of the fly ash-soil mixtures exhibiting the first flush behavior, the general observed trend was an exponential decay curve, as commonly seen in other CLT studies (Bin Shafique et al. 2007, Ram et al. 2007, Morar et al. 2010). The one exception to that trend was the arsenic concentrations for the C fly ash mixtures, which followed the initial decrease in concentration with a recovery in concentration. As a result of the typical first flush pattern, peak concentrations were generally measured at the start of the test. Consequently, in 70% of the CLTs, at least one metal was measured at the beginning of the test in concentrations above the appropriate regulatory limit. Effluent metal concentrations, however, in 80% of the columns tests decreased with time and stabilized around detection limits generally after 10-20 PV. The C fly ash columns seemed to show a more prolonged release of metal, with higher concentrations of metals measured for a longer duration of the test.

C fly ash mixtures also exhibited relatively constant pH values around 11.5 which supports the smoother leaching curves obtained from the C fly ash mixtures compared to large spikes in metal concentration seen in the BS fly ash mixtures, which also experienced pH fluctuations. CLT pH values were slightly lower than those of the WLTs, possibly due to the difference of contact time between solid media and leaching solution (Bin Shafique et al. 2007). Increased contact time in the WLT between leaching solution and solid phase mixture could allow for equilibrium to be more closely approached, or reached.

Overall, Cu levels for the S-C and C-C mixtures and As levels for the S-C mixture were elevated at intermediate pH (pH 7-9), and reduced at lower (pH \approx 5) and higher (pH \approx 11) pH values. However, As and Cr levels with the S-BS mixture showed an opposite trend, with reduced concentrations in the leachate at pH 7 and elevated levels at pH \approx 5 and pH \approx 9. In contrast, Cr levels with the C-C mixture exhibited a relatively flat pattern, with a gradual increase in Cr leachate concentration as the pH increased from \approx 5 to 11. The differences in leaching behavior for Cr as a function of pH for mixtures S-BS and C-C were largely a result of different Cr speciation (Cr(VI) in C fly ash and Cr(III) in BS fly ash) as well as the effect of higher clay content of the C soil that can lead to higher leaching through repulsion between metal ion and particle surface.

Clearly, the “leachability” of these elements is affected by many factors, including their solubility and adsorption capacity, the composition of coal ash, and the chemistry of the extracting water, including pH and ionic strength (Jo et al. 2008). More data from additional testing would be useful in confirming trends and predicting

leaching behavior based on pH measurements. Nevertheless, these results illustrate the significant effect that leachate pH can have on the leaching of heavy metals from fly ash-soil mixtures. A comparison of test results across a pH range from approximately 5-11 indicates that while leaching behavior varies by metal, under smaller pH ranges metal concentrations from some mixtures were found to be inversely proportional to the leachate pH (e.g., Cr leached from S-BS mixtures) which has been concluded in other soil-fly ash leaching studies (Bin Shafique et al. 2007, Ram et al. 2007, Palumbo et al. 2007).

The L:S ratio is second most important parameter behind pH in determining leaching behavior of heavy metals from amended soil media (Zandi and Russell, 2007). As discussed above, the majority of the CLT leaching curves exhibited first flush behavior, with leachate metal concentrations started high and sharply decreasing after several PV. Peak (typically initial) concentrations from the CLTs were typically higher than those of the TCLP and WLT batch tests, which is expected given the low L:S ratio present at start of CLTs. These CLT results are consistent with previous studies (Bin Shafique et al. 2007, Morar et al. 2010) and indicate that although leachate concentrations can initially exceed regulatory limits, this is observed for a short period of the leaching test and concentrations quickly decrease. Thus, while leachate concentrations from an embankment constructed with fly ash-amended soil might initially be measured at or above the regulatory limits, these elevated metal concentrations might only exist in the environment for a short period of time (i.e., hours to days), thereby reducing the overall risk of endangerment to aquatic and human health.

Increased fly ash content generally resulted in more metal leaching, although the rate of increase was not always uniform, nor was this trend observed in all sample mixtures and tests. For example, for Cu in S-BS TCLP mixtures, the difference in leachate concentrations between 10 and 20% fly ash was less compared to the initial addition of fly ash to the 100% soils (i.e., 0 to 10% fly ash), and the increase in fly ash content from 20% to 100%. This non-linear relationship makes simple estimations based solely on fly ash contents difficult and likely to either over- or underestimate actual metal concentrations in the leachate.

The test data also suggest that soil type has an importance influence on leaching. For example, TCLP Cr and Cu metal concentrations from soil S mixtures were 3-10 and 5-15 times higher, respectively, than the same mixtures with soil C. Similarly, WLT concentrations of Cu and Cr sometimes measured 10-30 µg/L higher in the soil S mixtures compared those with soil C. Soil C mixtures in the CLTs showed similar results with lower peak levels of aqueous metals measured compared to soil S mixtures, except for Cu in C-C-20 column. This is partly the result of different soil properties controlling adsorption onto particles surfaces and dissolution of minerals. The higher content of all metals in soil C, combined with lower observed leaching suggests that adsorption onto the finer particles in soil C was likely occurring and having a strong influence on leachate metal concentrations. Soils can be a sink through metal adsorption or a source through dissolution depending on pH conditions and the composition (metal content) of the other materials in the mixture, further complicating the leaching evaluation.

In summary, the key conclusions based on these results are as follows:

- 1) There exists a nonlinear relationship between leachate pH and fly ash content. As pH is one of the most important factors in determining metal leaching behavior, this relationship helps to explain differences in leaching between soil materials (C versus BS fly ash mixtures) and leaching tests (TCLP versus WLT). Processes that determine the final leachate pH are complex and vary both temporally and spatially within a soil column. Simple pH and oxidation-reduction potential measurements can serve as tools for predicting leachate metal species and their mobility and toxicity in the environment.
- 2) Although increased fly ash content may produce higher leaching of metals, the results of this study suggest that there is often a nonlinear relationship between leachate metal concentrations and fly ash content. For this reason, predictions of leaching based on simple dilution factors correcting for fly ash content are often not accurate and can under-predict actual metal concentrations (Bin Shafique et al. 2007). This potential for error highlights the need for reliable leaching protocols that can provide reasonable information necessary to determine risks associated with heavy metal leaching.
- 3) The chemical composition of the soil and the fly ash were key factors in determining leaching behavior by dictating the amount of available metal ions, the dominant species, and the location of metal ions on the particles (i.e., on the surface or embedded in mineral matrix). The distribution of metal species depends on the type of coal burned and the conditions of

combustion. When comparing the results of leaching tests, it is important to factor in higher initial metal contents in materials that exhibit increased leaching. Materials containing high original metal contents can become sources for dissolved metals, while materials with high adsorption capacities can provide sinks for dissolved metals and reduced aqueous metal concentrations.

- 4) There were instances in both the batch and column tests where leachate metal concentrations exceeded the corresponding regulatory limits for all three metals. However, caution should be exercised when applying leach test results to the development of CCB regulations and disposal guidelines. Batch tests do not always represent realistic field conditions while the typically high peaks seen at the beginning of CLTs are not representative of the long-term leaching risks.
- 5) Conducting CLTs with numerous samples of different soils and fly ashes would be impractical due to the long testing time needed and high costs of laboratory work. However, they provide useful insight into prolonged leaching as it would more likely occur in the field. Therefore, these tests should be included as part of a thorough investigation into leaching potential of any fly ash mixture.
- 6) TCLP leaching from the 100% soil and 100% fly ash samples provided upper and lower boundary limits for the leaching of fly ash-soil mixtures, as observed metal concentrations typically fell between these two. This trend was not as clearly observed in the WLTs, where levels of copper in

the 100% BS and C fly ashes and As in the 100% C fly ash were lower than in the soil-fly ash mixtures. A possible explanation of this is that precipitation and dissolution reactions can control metal concentrations when soil is not present (i.e., 100% fly ash samples). Soils provide an abundance of organic and inorganic ligands for complexation and precipitation and can increase soluble metal fractions.

- 7) Batch leach tests have an important role in the characterization of leaching behavior due to their short test duration, simple procedure, and relatively low costs. Efforts, however, should be taken to adjust test parameters to more reasonable values that better simulate the field. These adjustments could include reducing the L:S ratio to more accurately reflect average porosity and hydraulic conductivities in the constructed embankment or highway or changing the leaching solution used. Depending on the composition of the soils used, pH values could be adjusted to simulate a large carbonate content or the ionic strength increased to model groundwaters with a high salt content.

Appendix A: Tables and Figures

Table 2.1: Total elemental analysis results conducted on soils and fly ashes by University of Wisconsin Soil Testing and Plant Analysis Laboratories. All concentrations are reported as mg/kg dry weight except when stated otherwise.

Material	P (%)	K (%)	Ca (%)	Mg (%)	S (%)	Zn	B	Mn	Fe	Cu	Al	Na
BS FA	0.04	0.37	0.22	0.10	0.08	53.9	21.3	33.9	6400	59.6	21300	539
C FA	0.16	0.25	14.4	2.41	0.81	92.2	600	91.6	24400	189	91800	11200
Soil C	0.04	0.27	0.06	0.19	0.01	58.2	3.25	220	42200	27.2	49400	75
Soil S	0.02	0.05	0.03	0.04	0.01	15.0	2.86	38.2	10800	1.28	28800	33
Material	Cd	Co	Cr	Mo	Ni	Pb	Li	As	V	Ag	Sb	Tl
BS FA	0.42	20.9	49.5	11.7	21.3	23.0	35.7	24.2	78.8	0.001	0.05	<0.001
C FA	1.14	19.5	64.6	4.54	2.31	15.8	38.7	15.0	187	<0.001	0.06	<0.001
Soil C	<0.4	13.1	65.9	0.79	13.1	10.1	19.3	6.30	116	<0.001	0.02	<0.001
Soil S	<0.4	4.62	15.5	<0.4	<0.3	<2	4.02	<3	16.5	<0.001	0.02	<0.001

Table 2.2: Select chemical and physical properties of soils and fly ashes

Material	pH	Loss on Ignition	Classification	Atterberg Limits	Specific Gravity
Soil S	7.99	8.6%	SP-SC (poorly graded sand with silt) ²	N/A	2.6
Soil C	6.07	7.1%	SW-SC (well graded sand with clay & gravel) ²	37/21 ³	2.8
BS Fly Ash	4.98	5.5%	Off-spec ¹	N/A	2.3
C Fly Ash	12.11	0.4%	Class C ¹	N/A	2.7

Notes: ¹ASTM C816 classification; ²USCS classification; ³liquid limit/plastic limit

Table 2.3: Soil-fly ash mixture labels used in this study

Mixture Label	Fly Ash	Soil	% Fly Ash by Weight
S-BS-10	Brandon Shores	Soil S	10
S-BS-20	Brandon Shores	Soil S	20
S-C-10	Columbia	Soil S	10
S-C-20	Columbia	Soil S	20
C-BS-10	Brandon Shores	Soil C	10
C-BS-20	Brandon Shores	Soil C	20
C-C-10	Columbia	Soil C	10
C-C-20	Columbia	Soil C	20
BS FA	Brandon Shores	None	100
C FA	Columbia	None	100
Soil S	None	Soil S	0
Soil C	None	Soil C	0

Table 2.4: Properties of soil-fly ash mixtures obtained from preliminary compaction testing. This information was used in the setup of column leach tests to select compaction specifications of specimens.

Mixture	Optimum Moisture Content (%)	Dry Unit Weight (kN/m ³)	Pore Volume (mL)
S-BS-10	9	19.33	577
S-BS-20	11	18.65	622
S-C-10	11	18.94	643
S-C-20	13	18.79	665
Soil S	11	13.42	1171
C-BS-20	16	16.27	953
C-C-20	11	18.65	622

Table 3.1: pH measurements and concentrations of leachate Cu, Cr, and As from Water Leach Tests on soils, fly ashes, and soil-fly ash mixtures. EPA MCLs and Maryland freshwater Aquatic Toxicity limits are provided for comparison. Concentrations are averages of 4 replicates for fly ash-soil mixtures, 3 replicates for fly ash, and 2 replicates for soil.

Soil	Fly Ash	Fly Ash Content (%)	Leachate pH	Metal Concentration (µg/L)		
				Cu	Cr	As
Soil S	Columbia	10	11.6	7.6	57	0.90
		20	11.6	4.4	66	0.64
	Brandon Shores	10	6.7	1.7	<0.35	0.29
		20	6.0	3.9	<0.35	0.72
Soil C	Columbia	10	11.3	12	69	1.2
		20	11.5	14	100	0.63
	Brandon Shores	10	6.2	1.9	1.4	0.40
		20	6.6	3.9	1.2	0.38
Soil S	None	0	5.8	1.4	0.90	<0.22
Soil C	None	0	8.7	2.6	0.36	<0.22
None	Columbia	100	11.9	2.0	45	0.35
	Brandon Shores	100	8.8	2.6	2.8	23
U.S. EPA Drinking Water MCL				1300	100	10
Maryland State Aquatic Toxicity Acute Limits				13	570/16*	340
Maryland State Aquatic Toxicity Chronic Limits				9	74/11*	150

*regulation limits for chromium given as [Cr III]/[Cr VI]

Table 3.2: pH measurements and concentrations of leachate Cu, Cr, and As from Toxicity Characteristic Leaching Procedure Tests on soils, fly ashes, and soil-fly ash mixtures. EPA MCLs and Maryland freshwater Aquatic Toxicity limits are provided for comparison. Concentrations are averages of 4 replicates for fly ash-soil mixtures, 3 replicates for fly ash, and 2 replicates for soil.

Soil	Fly Ash	Fly Ash Content (%)	Leachate pH	Metal Concentration (µg/L)		
				Cu	Cr	As
Sandy	Columbia	10	5.2	11	20	<.49
		20	5.5	5.3	30	1.3
	Brandon Shores	10	4.9	29	8.0	1.0
		20	4.8	26	17	3.0
Clayey	Columbia	10	5.2	7.6	25	<.49
		20	5.5	7.3	54	<.49
	Brandon Shores	10	4.8	1.8	2.5	1.1
		20	4.8	4.7	7.3	0.49
Sandy	None	0	4.8	<1.4	<1.8	<.49
Clayey	None	0	4.8	<1.4	<1.8	1.7
None	Columbia	100	6.3	<1.4	140	30
	Brandon Shores	100	4.9	93	45	85
U.S. EPA Drinking Water MCL				1300	100	10
Maryland State Aquatic Toxicity Acute Limits				13	570/16*	340
Maryland State Aquatic Toxicity Chronic Limits				9	74/11*	150

*regulation limits for chromium given as [Cr III]/[Cr VI]

Table 3.3: pH measurements and Cu, Cr, and As leachate concentrations for buffered water leach tests. The water leach test procedure was performed twice for each mixture using each of the two buffers used (BES and CAPSO). Concentrations are reported as µg/L. Concentrations below detection limit for Cr (0.35 µg/L) and As (0.22 µg/L) are reported as ½ of the detection limit.

Mixture	Buffer	pH	[Cu]	[Cr]	[As]
S-BS-10 1	BES	6.99	42.9	0.175	0.634
S-BS-10 2	BES	6.99	41.8	0.175	0.253
S-BS-10 3	CAPSO	9.01	1.23	1.74	4.79
S-BS-10 4	CAPSO	9.00	3.19	6.23	4.31

S-C-10 1	BES	7.23	66.5	22.3	2.66
S-C-10 2	BES	7.20	63.4	10.8	2.31
S-C-10 3	CAPSO	9.29	50.7	54.3	2.89
S-C-10 4	CAPSO	9.28	49.6	52.3	2.81

S-BS-20 1	BES	6.95	47.0	0.175	1.77
S-BS-20 2	BES	6.97	46.1	0.175	1.69
S-BS-20 3	CAPSO	9.09	2.50	3.43	8.94
S-BS-20 4	CAPSO	9.11	5.46	3.86	14.6

S-C-20 1	BES	7.34	78.9	29.0	8.84
S-C-20 2	BES	7.32	79.2	29.2	10.0
S-C-20 3	CAPSO	9.46	87.0	19.8	3.57
S-C-20 4	CAPSO	9.44	81.2	21.3	4.79

C-C-10 1	BES	7.24	55.2	33.8	0.438
C-C-10 2	BES	7.25	53.2	31.4	0.308
C-C-10 3	CAPSO	9.35	53.5	73.8	0.467
C-C-10 4	CAPSO	9.31	55.3	76.7	0.333

C-C-20 1	BES	7.44	28.0	54.0	0.789
C-C-20 2	BES	7.42	25.2	50.3	1.19
C-C-20 3	CAPSO	9.45	64.4	112	0.498
C-C-20 4	CAPSO	9.49	72.1	117	0.762

C-BS-10 1	BES	7.06	31.6	1.67	0.110
C-BS-10 2	BES	7.05	12.3	1.31	0.110
C-BS-10 3	CAPSO	8.77	2.00	4.68	0.359
C-BS-10 4	CAPSO	8.77	2.74	4.50	0.518

C-BS-20 1	BES	7.04	27.4	1.71	0.110
C-BS-20 2	BES	7.03	24.4	1.57	0.110
C-BS-20 3	CAPSO	8.81	2.61	6.05	0.756
C-BS-20 4	CAPSO	8.79	2.64	7.35	1.07

Table 3.4: Comparison of leaching results from all three leaching tests conducted. Column leach test peak concentration is the highest measured concentration throughout the testing period. Column leach test MC concentrations are calculated based on a liquid-to-solid ratio of 5 and represent a volume-weighted average concentration. Concentrations are all reported as µg/L. N/A listed for the column leach tests indicate that that specific mixture was not tested using the CLT methodology.

	TCLP			WLT			CLT - Peak Conc.			CLT - L:S Ratio MC		
Mixture	Cu	As	Cr	Cu	As	Cr	Cu	As	Cr	Cu	As	Cr
Soil S	<1.4	<.49	<1.8	1.4	<.22	0.90	12	0.62	160	1.7	0.28	9.9
S-BS-10	29	1.0	8.0	1.7	0.29	<.35	21	0.89	67	1.6	0.26	8.4
S-BS-20	26	3.0	17	3.9	0.72	<.35	12	3.1	250	1.3	0.97	21
S-C-10	11	<.49	20	7.6	0.9	57	83	3.8	290	7.5	1.9	44
S-C-20	5.3	1.3	30	4.4	0.64	66	35	3.5	270	5.5	1.6	36
Soils C	<1.4	1.7	<1.8	2.6	<.22	0.36	N/A	N/A	N/A	N/A	N/A	N/A
C-BS-10	1.8	1.1	2.5	1.9	0.4	1.4	N/A	N/A	N/A	N/A	N/A	N/A
C-BS-20	4.7	0.49	7.3	3.9	0.38	1.2	7.6	1.7	20	1.5	0.45	1.1
C-C-10	7.6	<.49	25	12	1.2	69	N/A	N/A	N/A	N/A	N/A	N/A
C-C-20	7.6	<.49	54	14	0.63	100	110	2.0	240	26	1.4	88
C FA	<1.4	30	140	2	0.35	45	N/A	N/A	N/A	N/A	N/A	N/A
BS FA	93	85	45	2.6	23	2.8	N/A	N/A	N/A	N/A	N/A	N/A

Table 3.5: Estimated scaling factors based on ratio of column leach test metal concentrations to water leach test metal concentrations. Part (a) uses peak column leach test concentrations while part (b) uses the volume-weighted average concentration up to a liquid-to-solid ratio of 5:1. An asterisk indicates that the scaling factor for Cr is based on a water leach test concentration of 0.35 µg/L since measured concentrations for these mixtures were below this detection limit.

(a) Peak CLT

Mixture	Cr	Cu	As
S-BS-10*	191	12.4	3.1
S-BS-20*	714	3.1	4.3
S-C-10	5.1	10.9	4.2
S-C-20	4.1	8.0	5.5
C-BS-20	16.7	1.9	4.5
C-C-20	2.4	7.9	3.2

(b) Mean CLT

Mixture	Cr	Cu	As
S-BS-10*	24.0	0.9	0.9
S-BS-20*	60.0	0.3	1.3
S-C-10	0.8	1.0	2.1
S-C-20	0.5	1.3	2.5
C-BS-20	0.9	0.4	1.2
C-C-20	0.9	1.9	2.2

Table 3.6: Leachate metal concentrations representing a 100% leaching scenario based on a mass-weighted average of original material metal content. Concentrations are reported in mg/kg dry weight.

Mixture	Maximum [Cu]	Maximum [Cr]	Maximum [As]
S-BS-10	7.12	18.9	5.12
S-BS-20	13.0	22.3	7.23
S-C-10	20.0	20.4	4.20
S-C-20	38.7	25.3	5.40
C-BS-10	30.4	64.3	8.09
C-BS-20	33.7	62.7	9.87
C-C-10	43.3	65.8	7.17
C-C-20	59.4	65.7	8.04

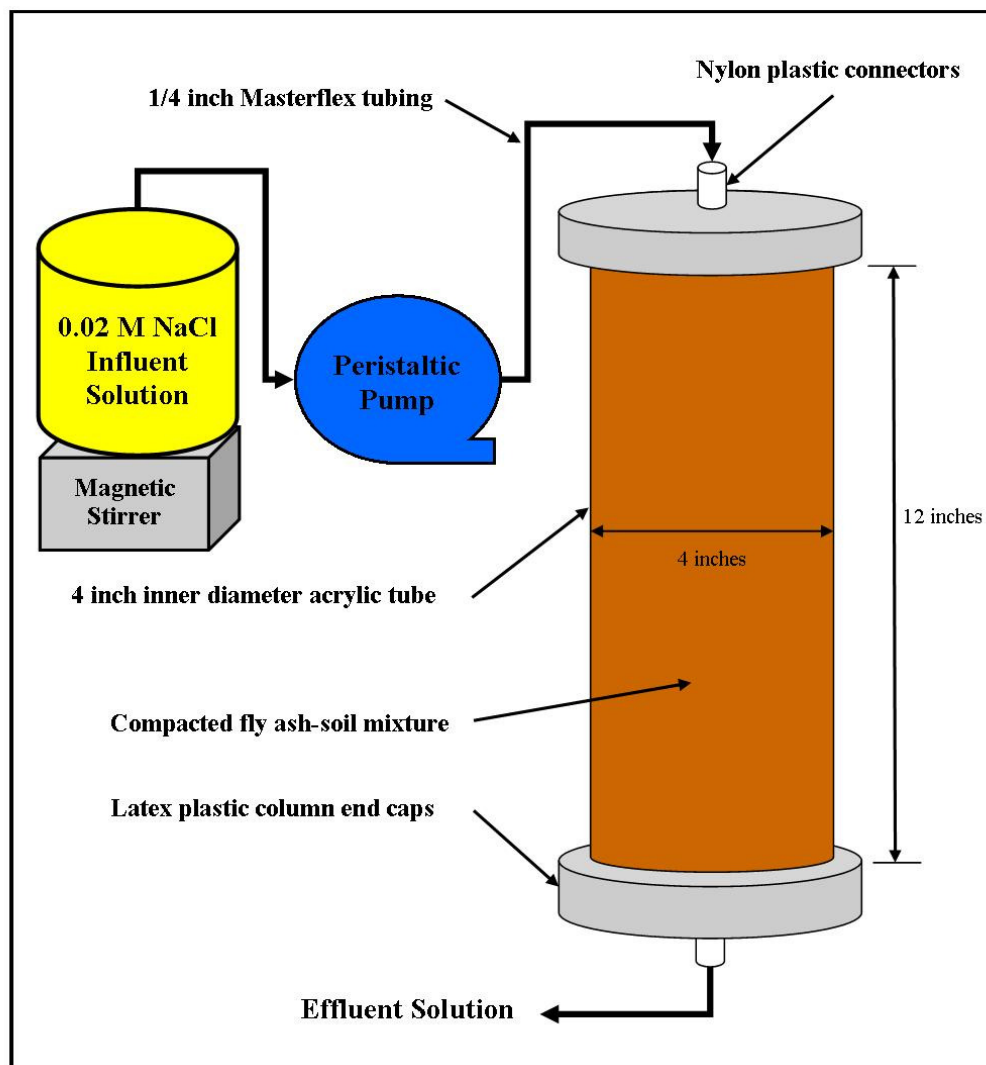


Figure 2.1: Schematic of experimental setup for column leach test.

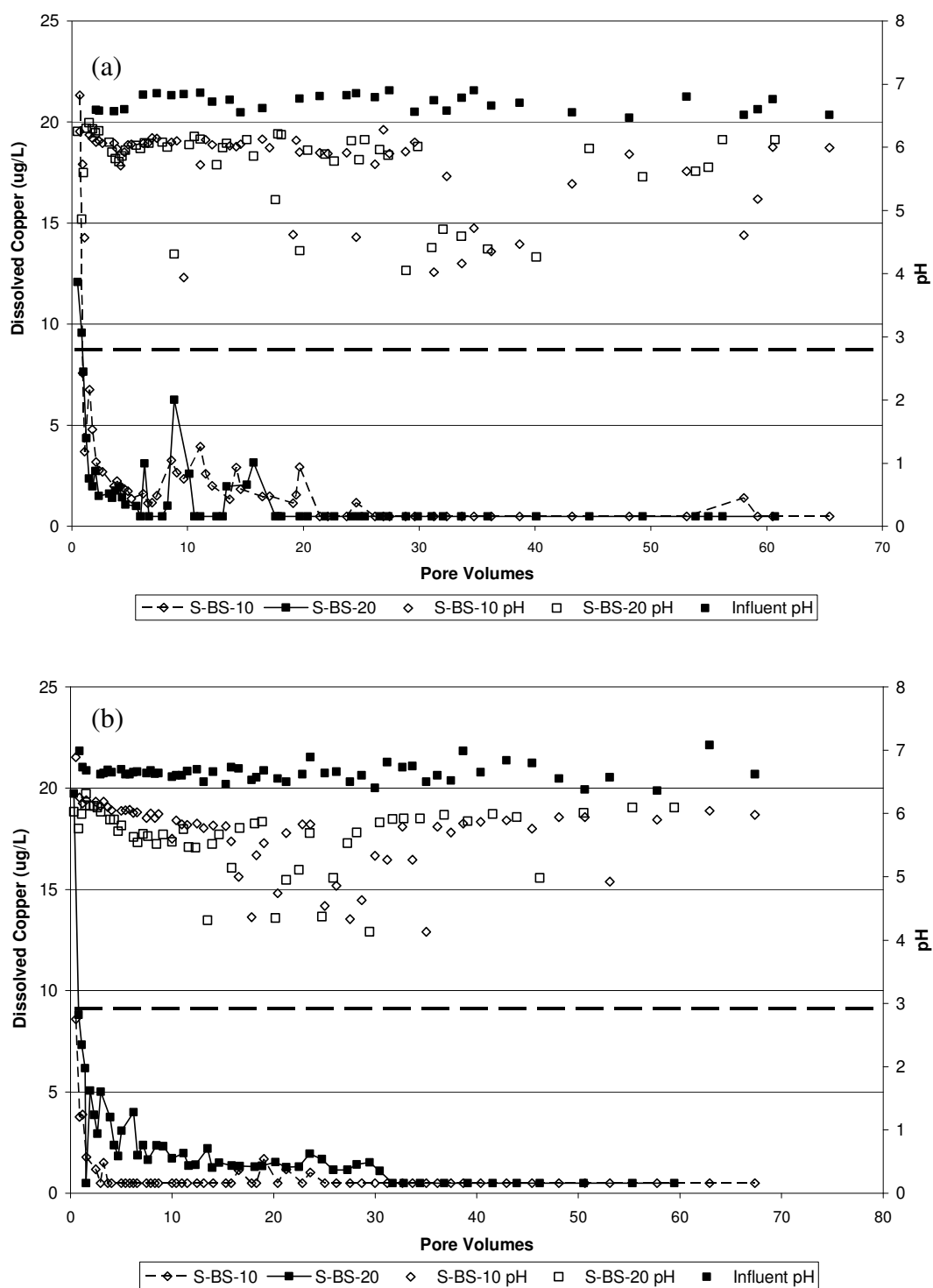


Figure 3.1: Copper leachate concentrations from: (a) the 1st set of column leach test S-BS mixtures, and (b) the 2nd set of column leach test S-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 1.0 $\mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit. Dashed lines represent Aquatic Toxicity limit of 9 $\mu\text{g/L}$.

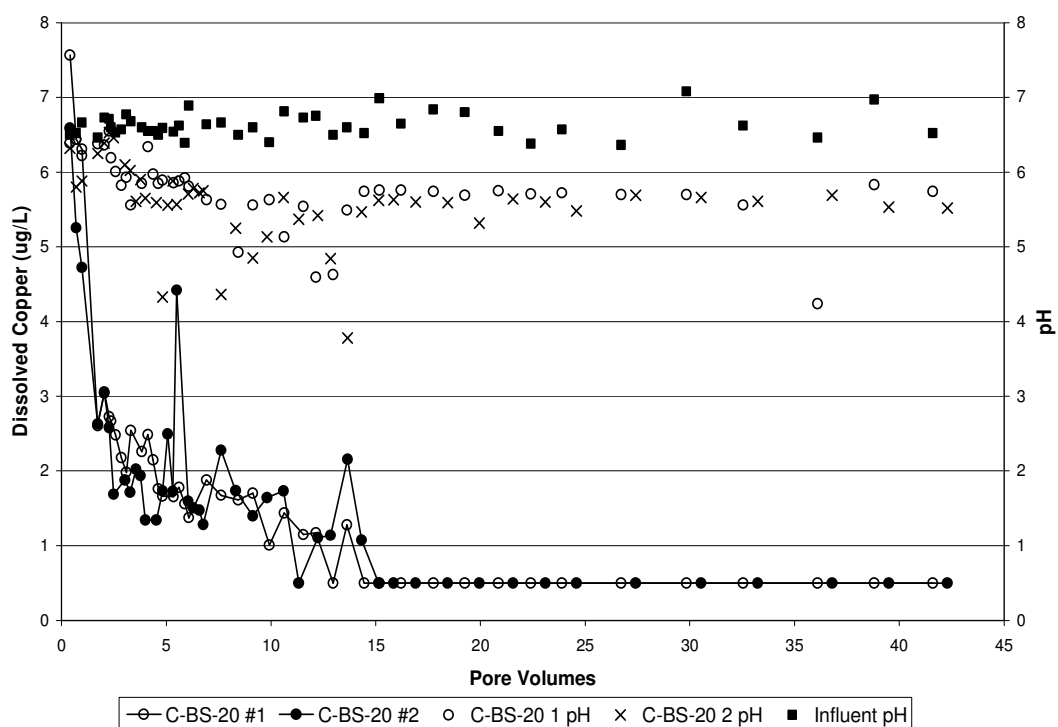


Figure 3.2: Copper leachate concentrations from column leach test C-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations $< 1.0 \mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit.

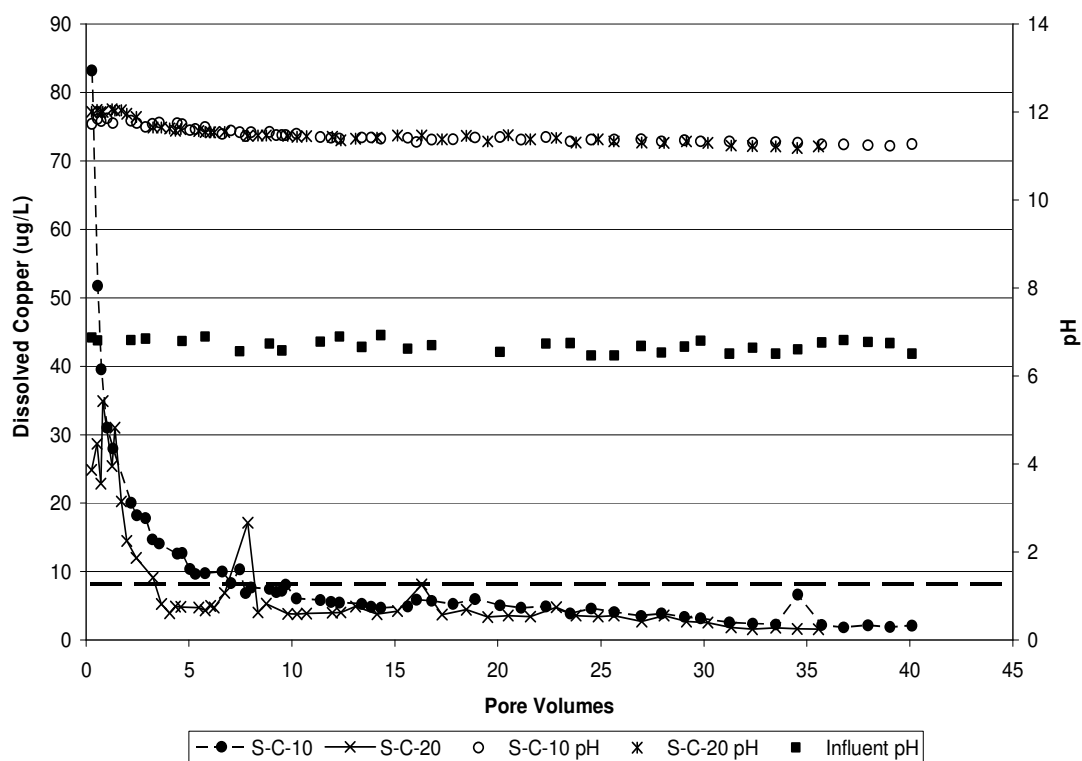


Figure 3.3: Copper leachate concentrations from the column leach test S-C mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 1.0 µg/L were reported as ½ of the detection limit. Dashed line represents Aquatic Toxicity limit of 9 µg/L.

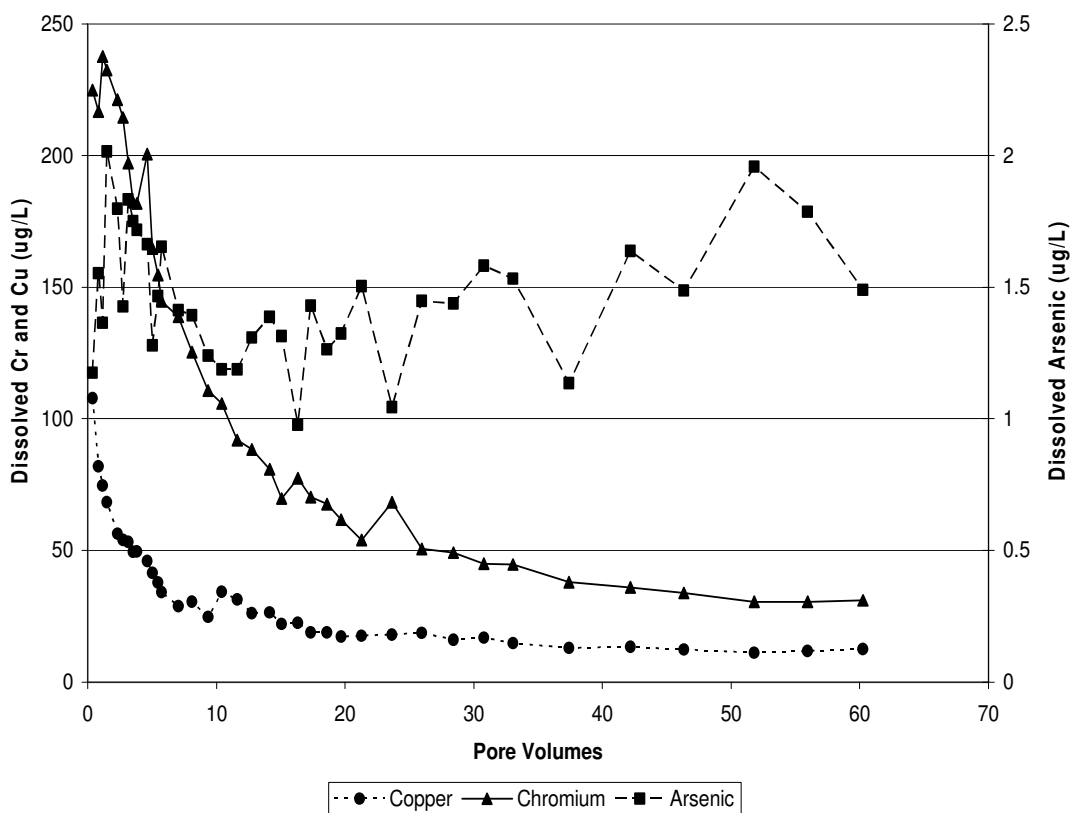


Figure 3.4: Copper, chromium, and arsenic leachate concentrations from column leach test C-C-20 mixture. Each symbol represents the average of two sample replicate metal measurements. The regulatory limits were 100 $\mu\text{g/L}$ for Cr, 9 $\mu\text{g/L}$ for Cu, and 10 $\mu\text{g/L}$ for As.

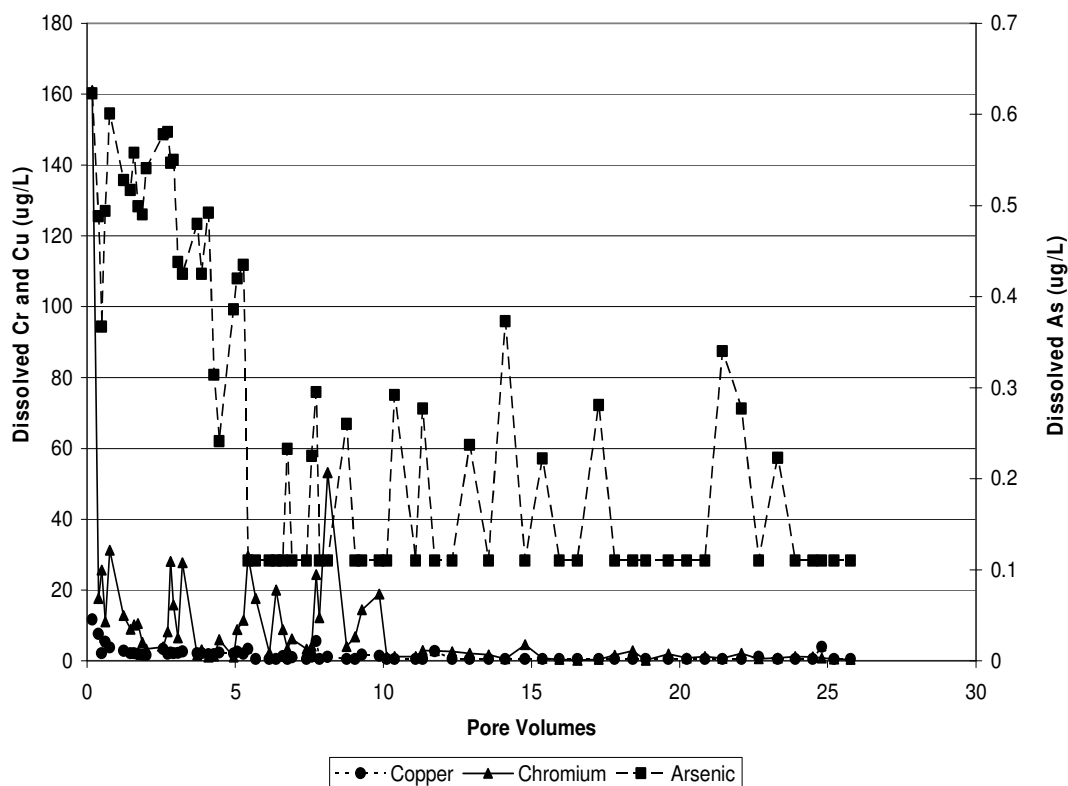


Figure 3.5: Copper, chromium, and arsenic leachate concentrations from column leach test 100% soil S mixture. Each symbol represents the average of two sample replicate metal measurements. The regulatory limits were 100 $\mu\text{g/L}$ for Cr, 9 $\mu\text{g/L}$ for Cu, and 10 $\mu\text{g/L}$ for As.

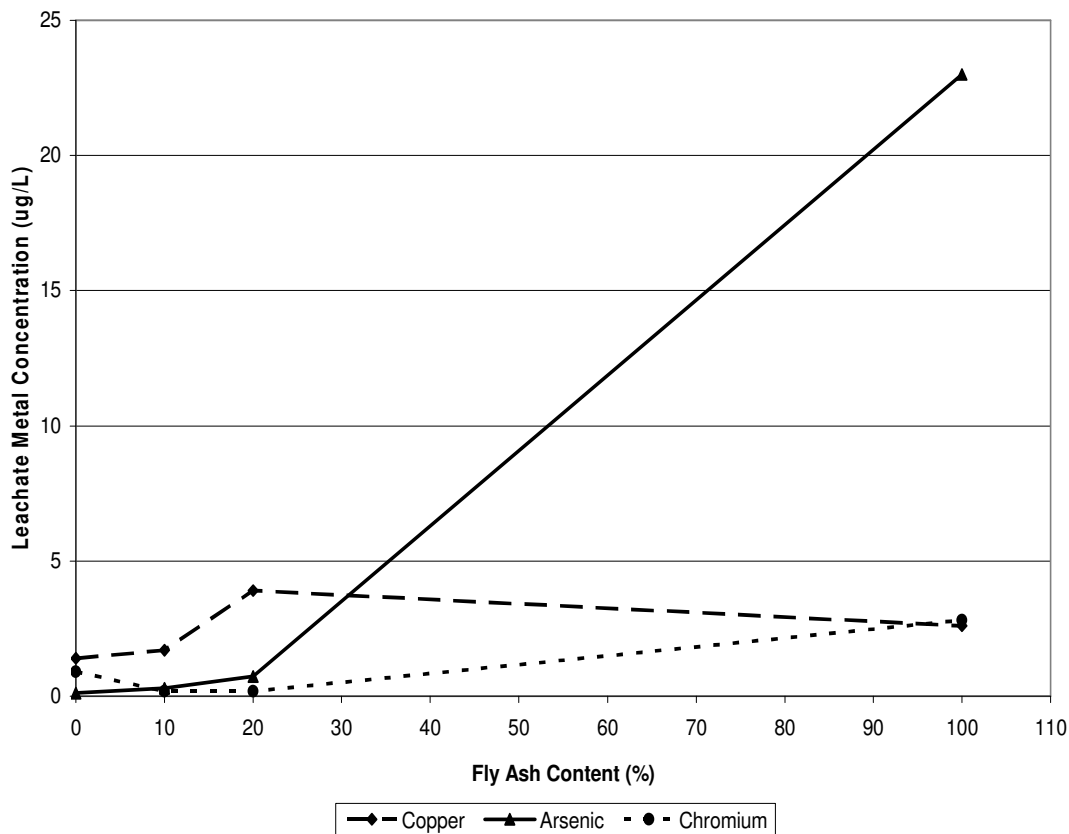


Figure 3.6: Effect of fly ash content on leachate metal concentrations for water leach test S-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-BS-10 mixture are 7.12, 18.9, and 5.12 $\mu\text{g/L}$ and for the S-BS-20 mixture are 13.0, 22.3, and 7.23 $\mu\text{g/L}$ for Cu, Cr, and As, respectively.

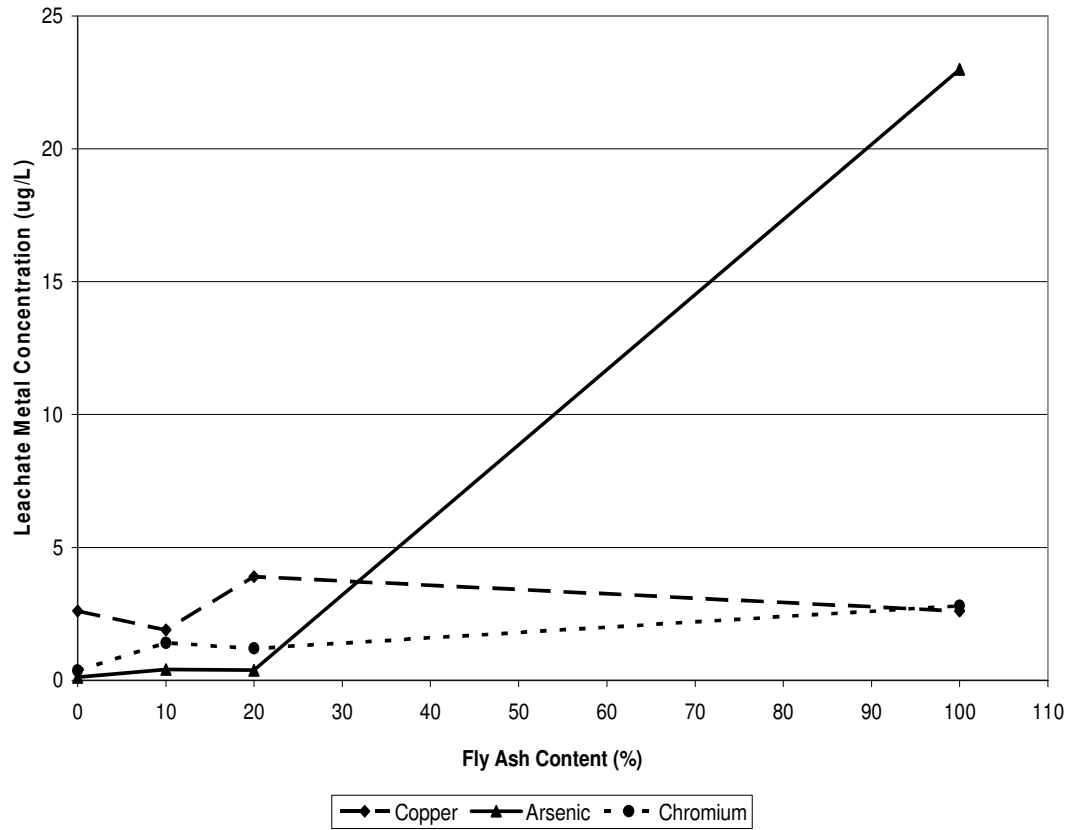


Figure 3.7: Effect of fly ash content on leachate metal concentrations for water leach test C-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-BS-10 mixture are 30.4, 64.3, and 8.09 $\mu\text{g/L}$ and for the C-BS-20 mixture are 33.7, 62.7, and 9.87 $\mu\text{g/L}$ for Cu, Cr, and As, respectively.

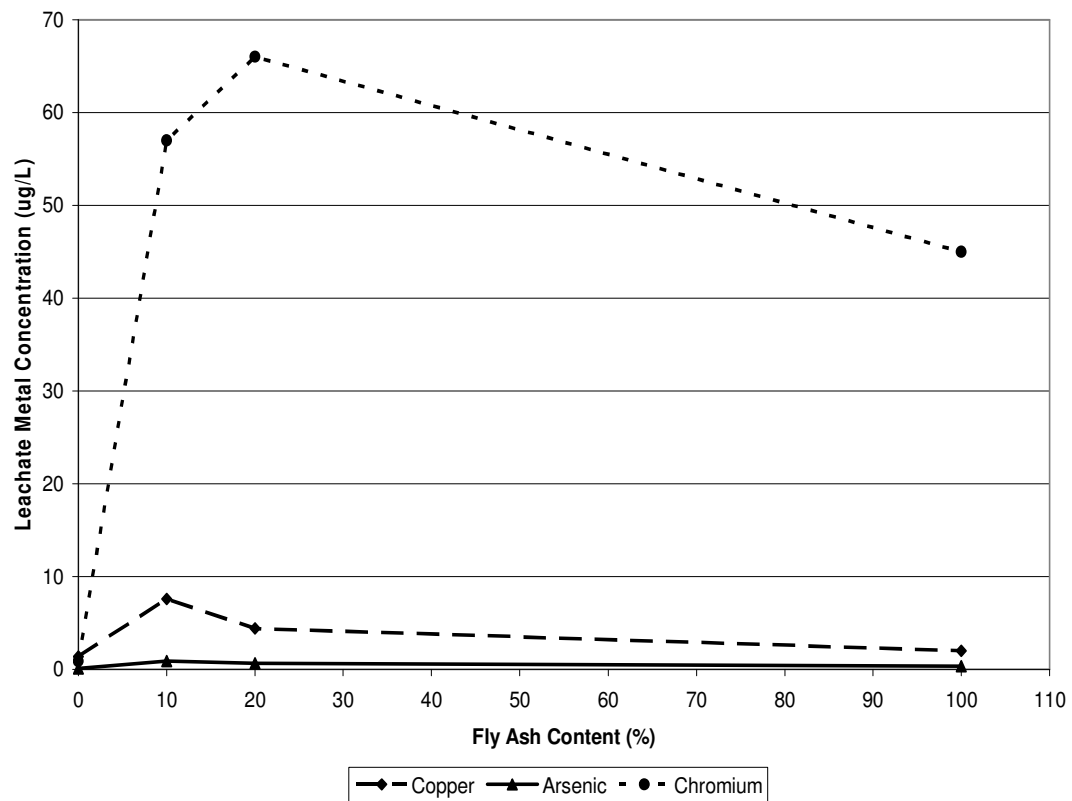


Figure 3.8: Effect of fly ash content on leachate metal concentrations for water leach test S-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-C-10 mixture are 20.0, 20.4, and 4.20 µg/L and for the S-C-20 mixture are 38.7, 25.3, and 5.40 µg/L for Cu, Cr, and As, respectively.

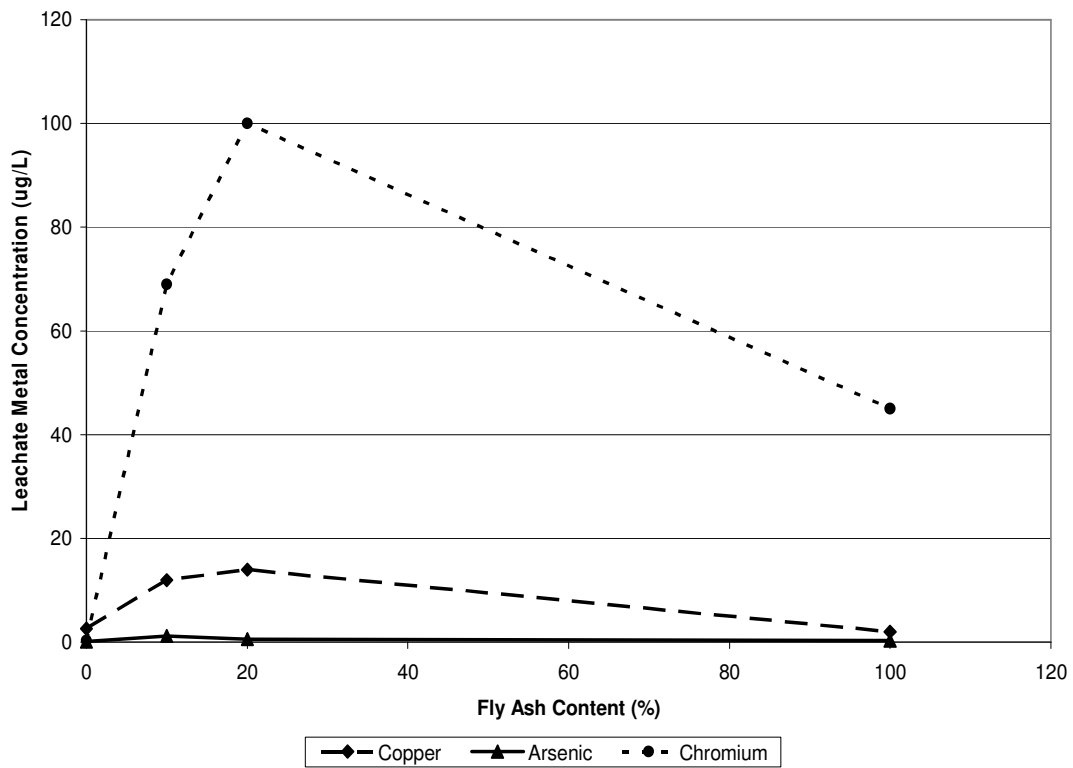


Figure 3.9: Effect of fly ash content on leachate metal concentrations for water leach test C-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-C-10 mixture are 43.3, 65.8, and 7.17 $\mu\text{g/L}$ and for the C-C-20 mixture are 59.4, 65.7, and 8.04 $\mu\text{g/L}$ for Cu, Cr, and As, respectively.

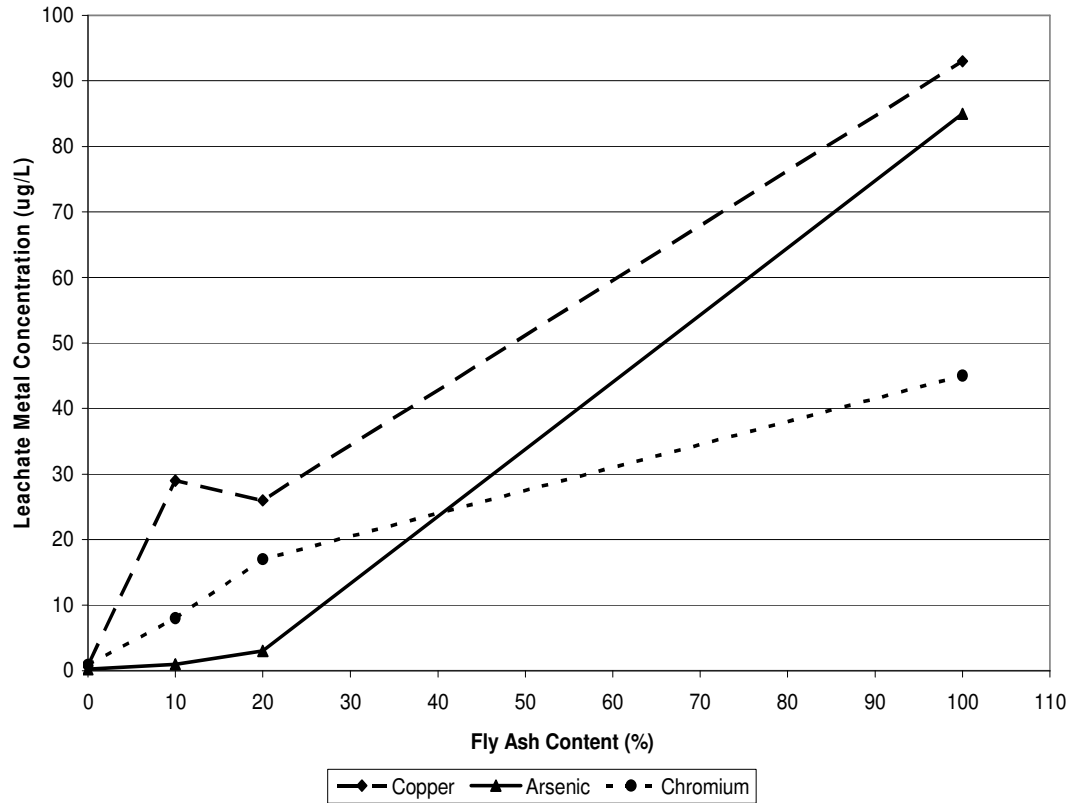


Figure 3.10: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure S-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-BS-10 mixture are 7.12, 18.9, and 5.12 µg/L and for the S-BS-20 mixture are 13.0, 22.3, and 7.23 µg/L for Cu, Cr, and As, respectively.

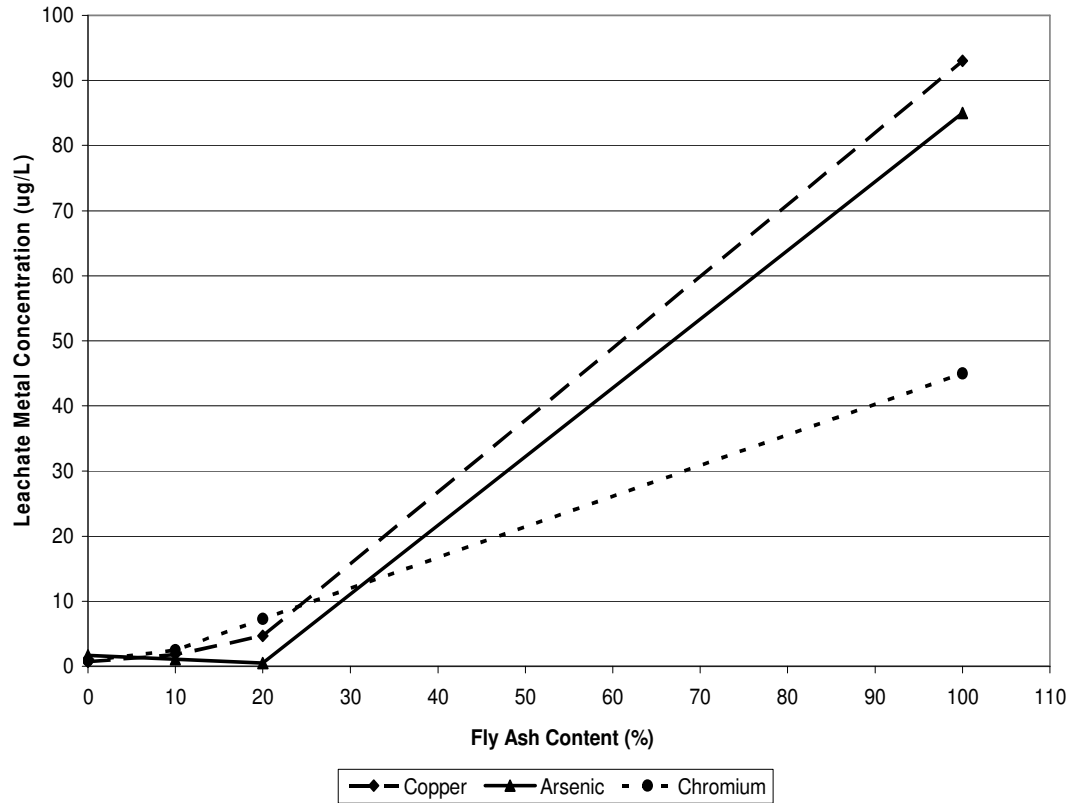


Figure 3.11: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure C-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-BS-10 mixture are 30.4, 64.3, and 8.09 $\mu\text{g/L}$ and for the C-BS-20 mixture are 33.7, 62.7, and 9.87 $\mu\text{g/L}$ for Cu, Cr, and As, respectively.

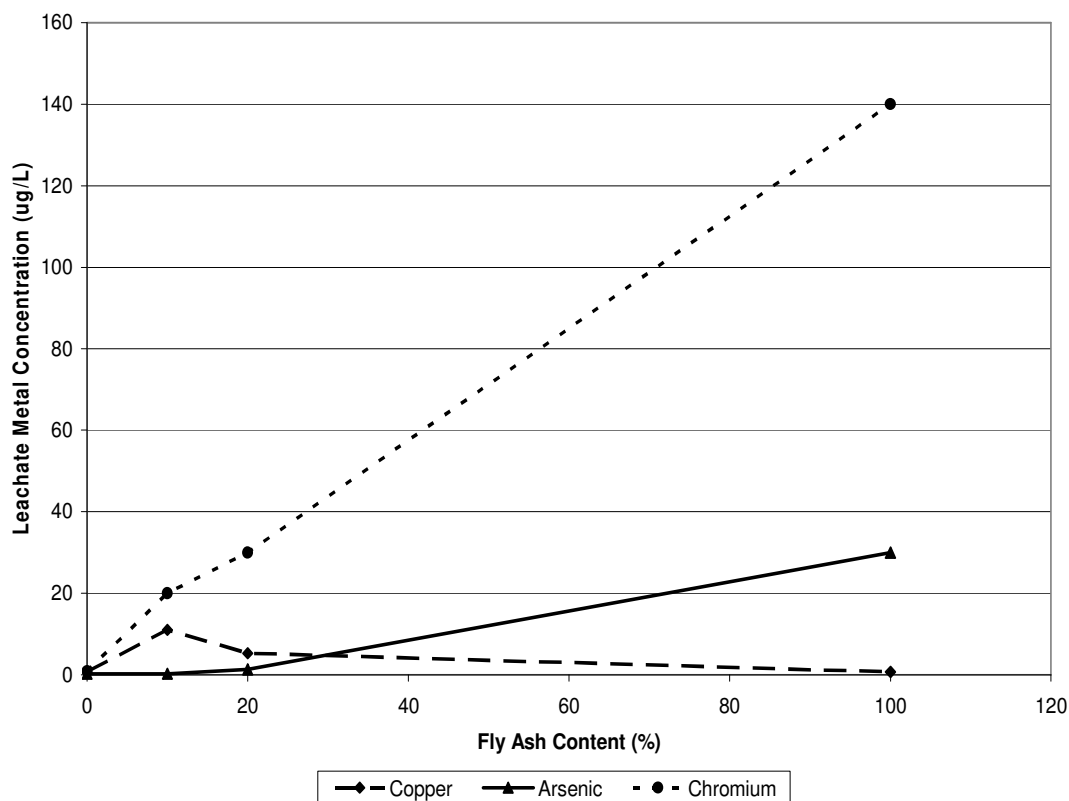


Figure 3.12: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure S-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-C-10 mixture are 20.0, 20.4, and 4.20 $\mu\text{g/L}$ and for the S-C-20 mixture are 38.7, 25.3, and 5.40 $\mu\text{g/L}$ for Cu, Cr, and As, respectively.

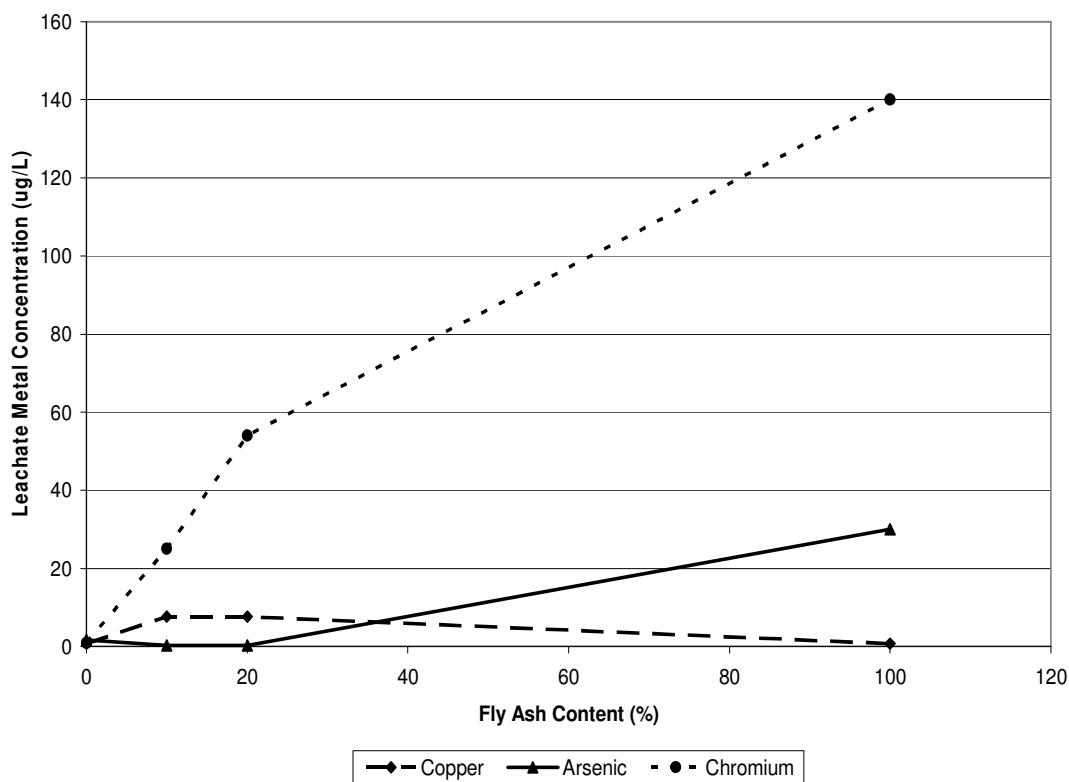


Figure 3.13: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure C-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-C-10 mixture are 43.3, 65.8, and 7.17 $\mu\text{g/L}$ and for the C-C-20 mixture are 59.4, 65.7, and 8.04 $\mu\text{g/L}$ for Cu, Cr, and As, respectively.

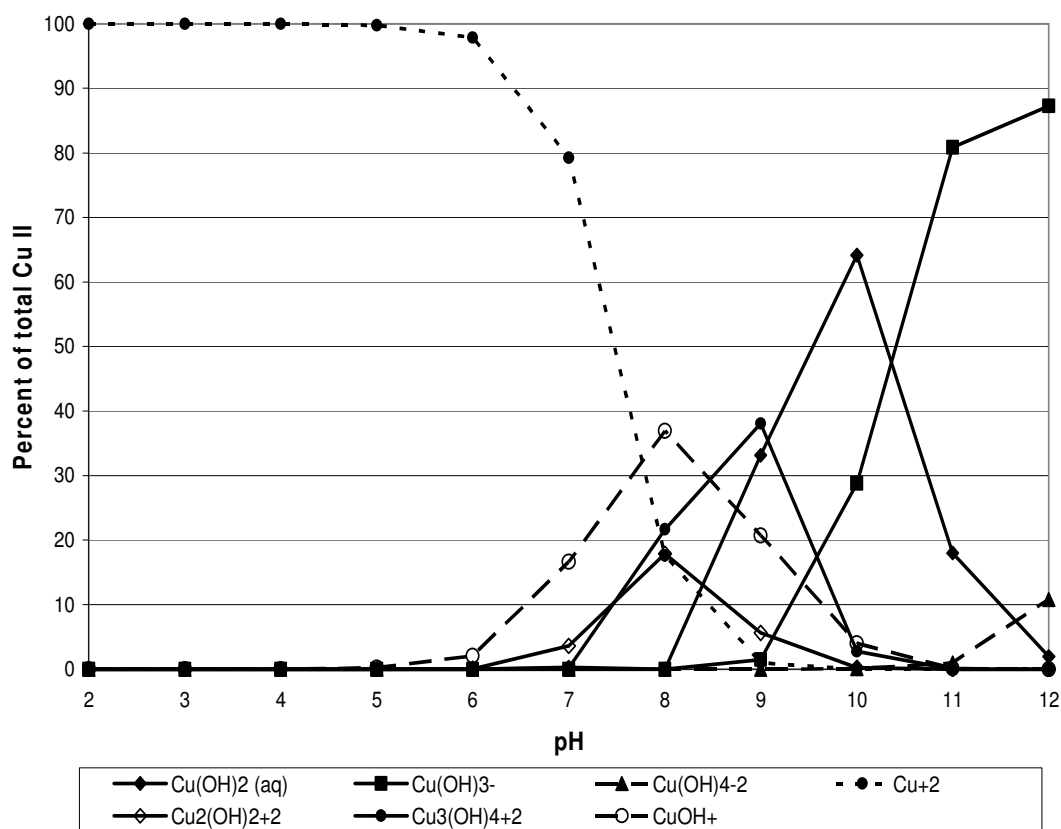


Figure 3.14: Effect of pH on Cu(II) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total Cu(II) concentration of 1 mg/L. Notice the rise in dominance of the neutral and then anionic forms of Cu as the pH increases.

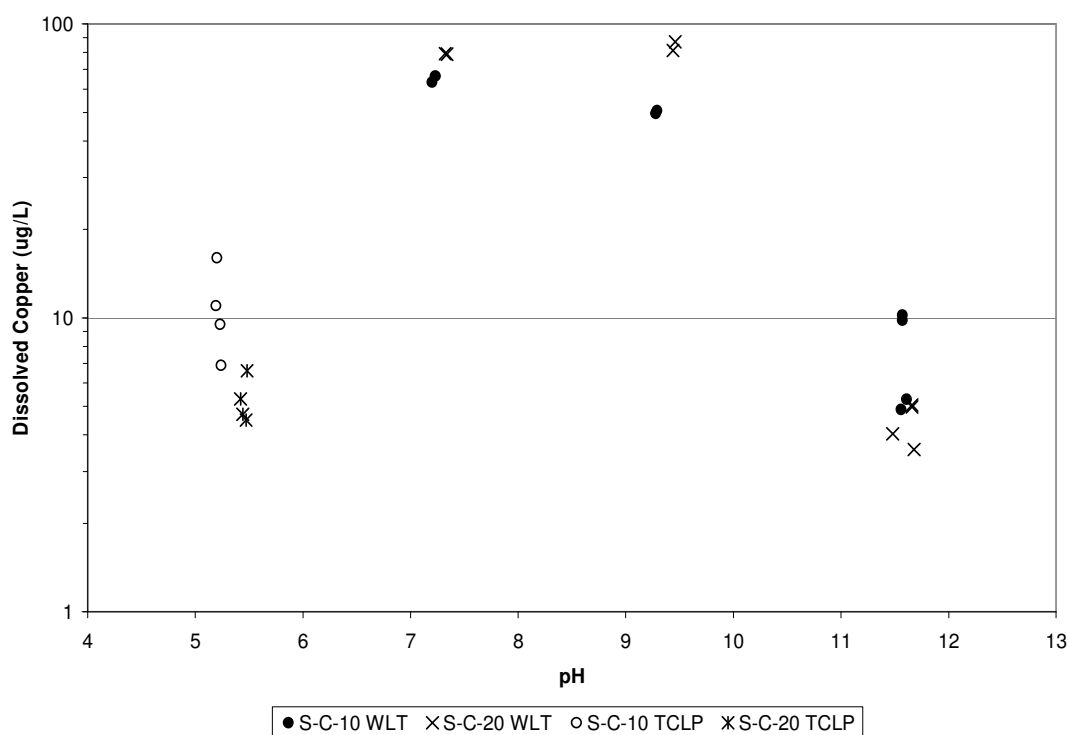


Figure 3.15: Effect of pH on leachate copper concentrations for S-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Lower concentrations around pH 11.5 could reflect precipitation likely under alkaline conditions, while higher concentrations measured around neutral pH suggest complexation with soil organic matter could maintain soluble metal in the leachate.

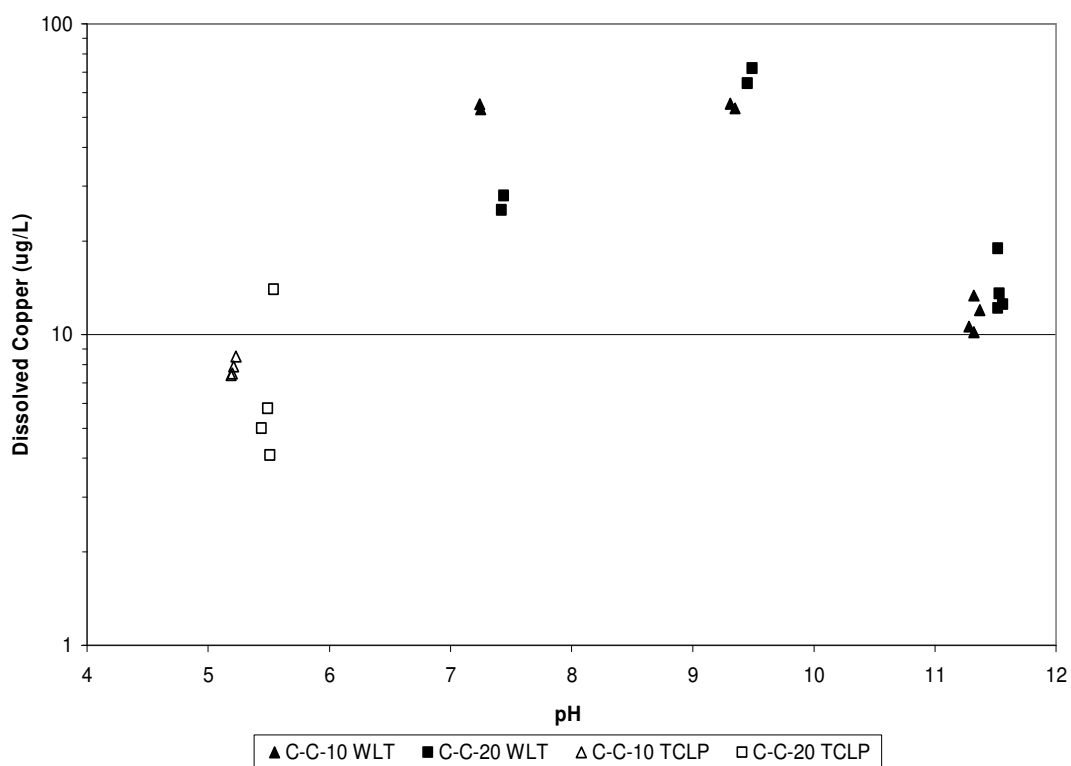


Figure 3.16: Effect of pH on leachate copper concentrations for C-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Soil organic matter is likely responsible for the higher leachate concentrations measured around pH 7-8 through complexation processes.

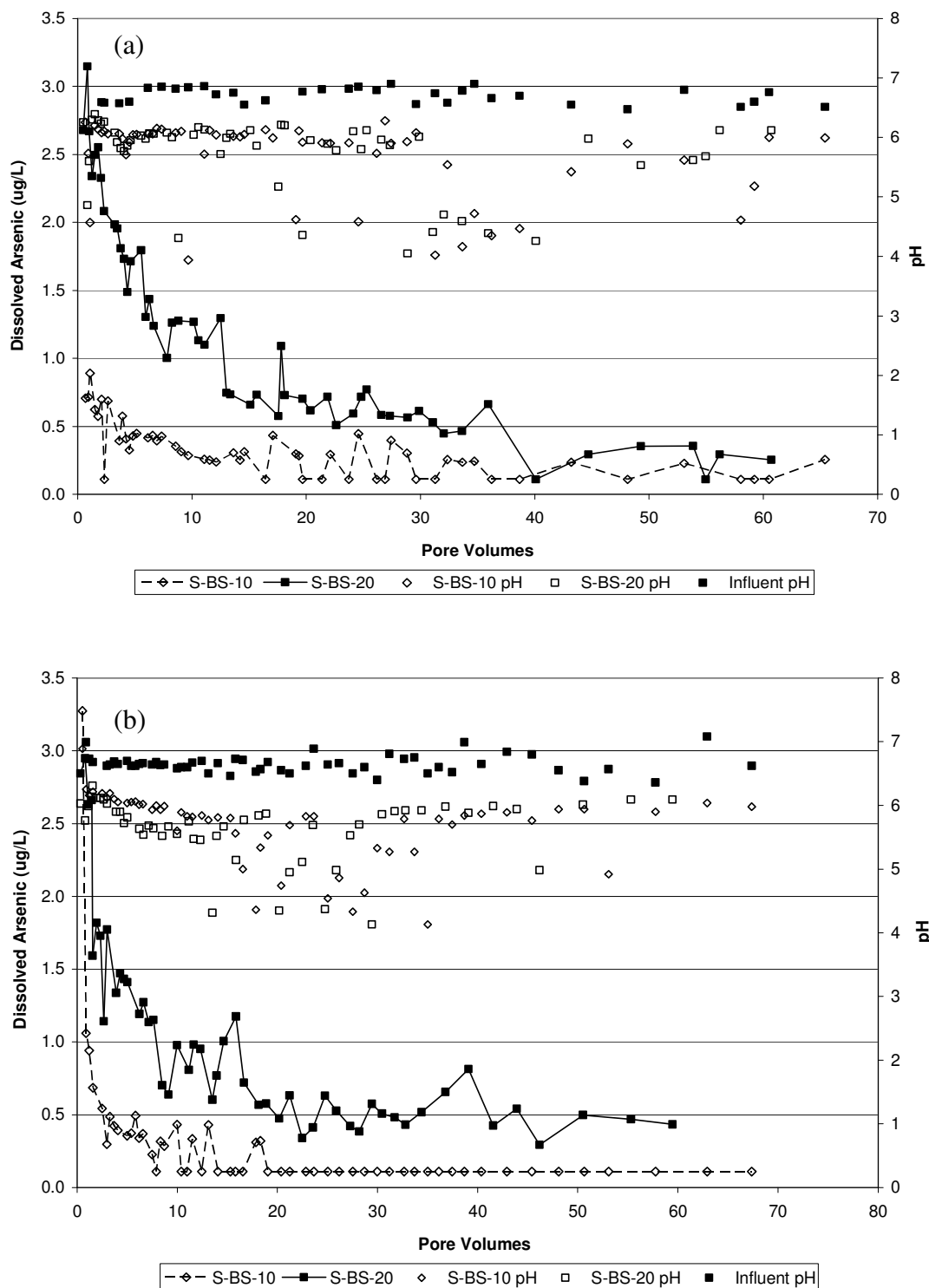


Figure 3.17: Arsenic leachate concentrations from: (a) the 1st set of column leach test S-BS mixtures, and (b) the 2nd set of column leach test S-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.22 ug/L were reported as ½ of the detection limit.

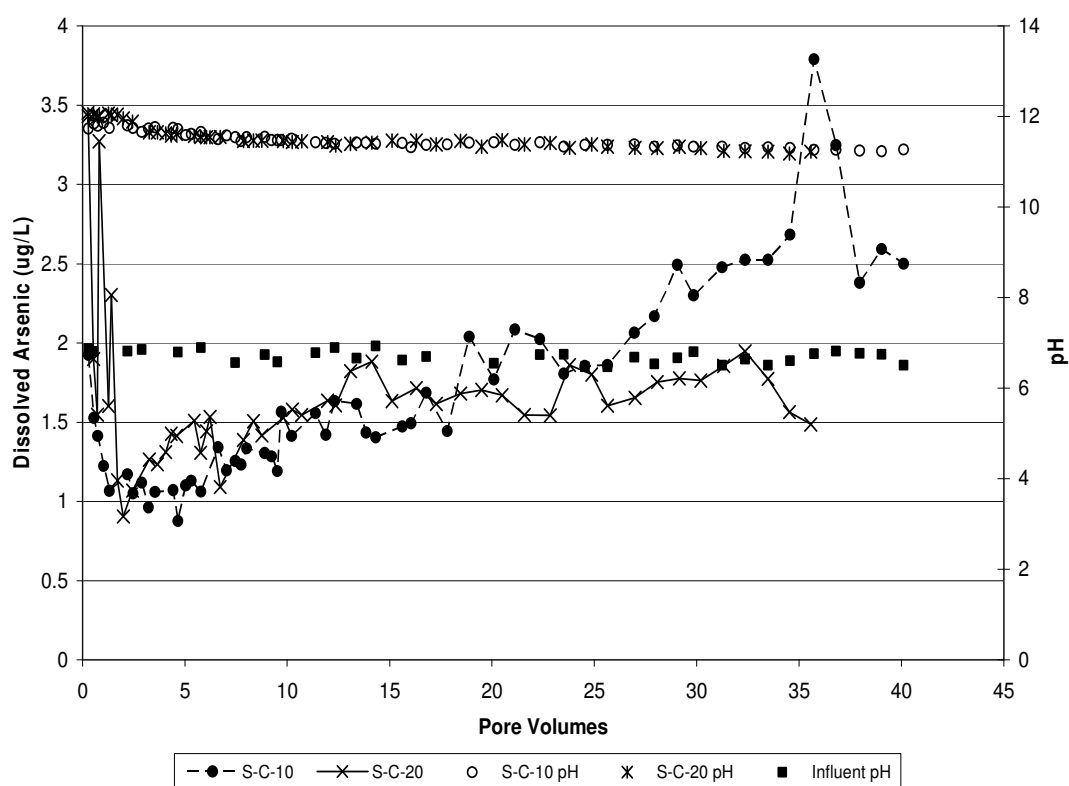


Figure 3.18: Arsenic leachate concentrations from column leach test S-C mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.22 $\mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit.

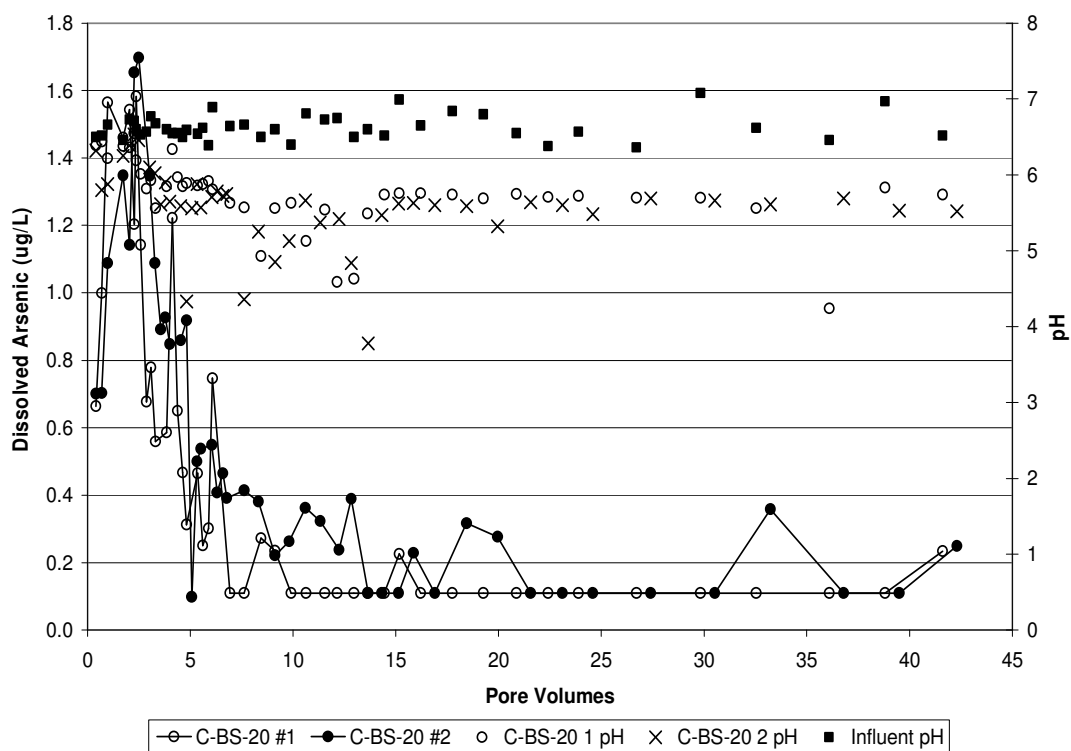


Figure 3.19: Arsenic leachate concentrations from column leach test C-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.22 $\mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit.

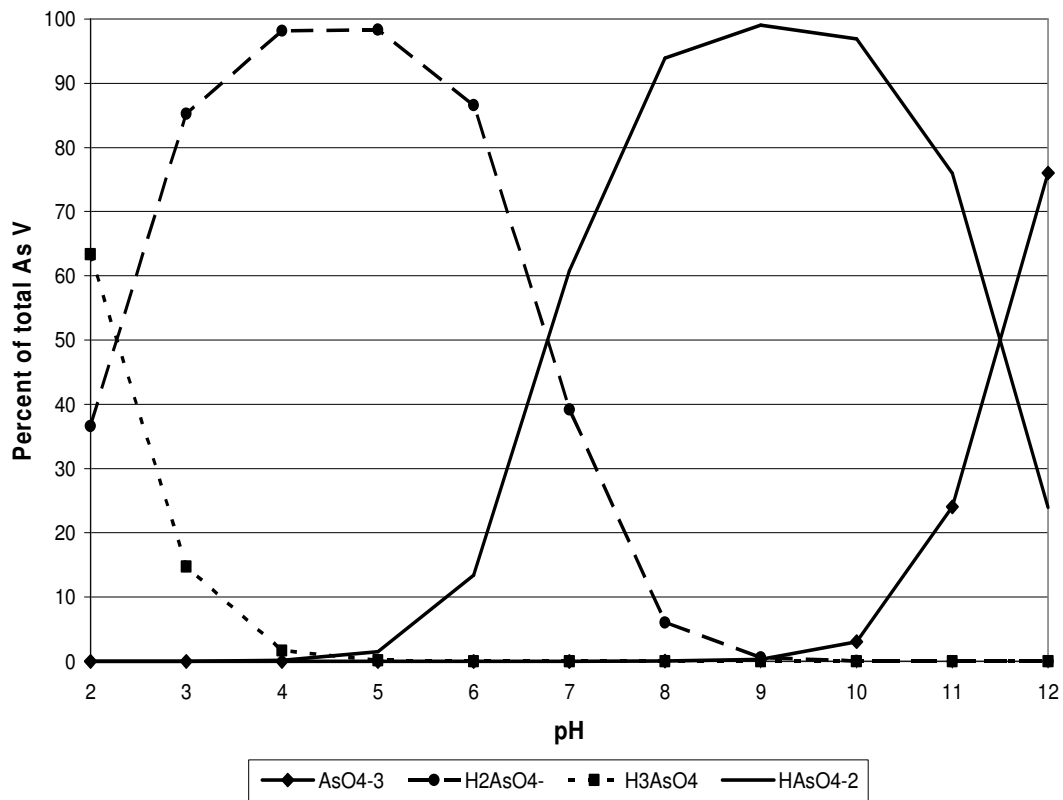


Figure 3.20: Effect of pH on As(V) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total As(V) concentration of 1 mg/L.

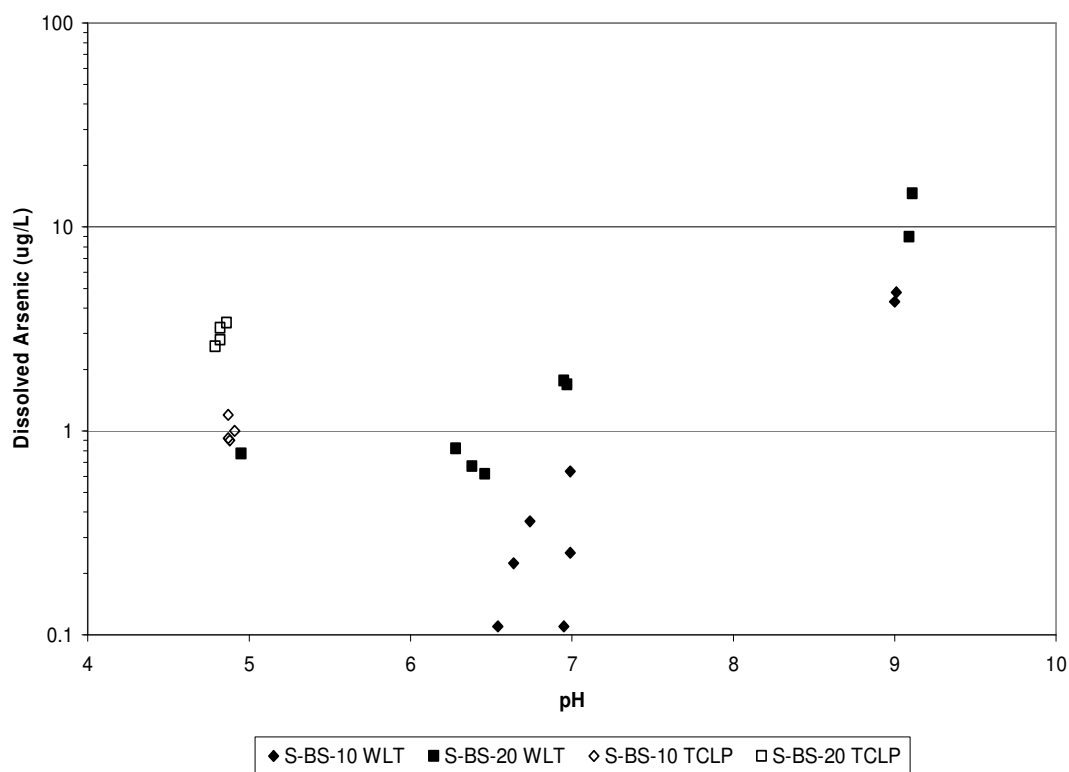


Figure 3.21: Effect of pH on leachate arsenic concentrations for S-BS mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Generally the As concentrations are below the EPA MCL of 10 $\mu\text{g/L}$ except around pH 9, which could be due to repulsion of anionic As species under more basic conditions.

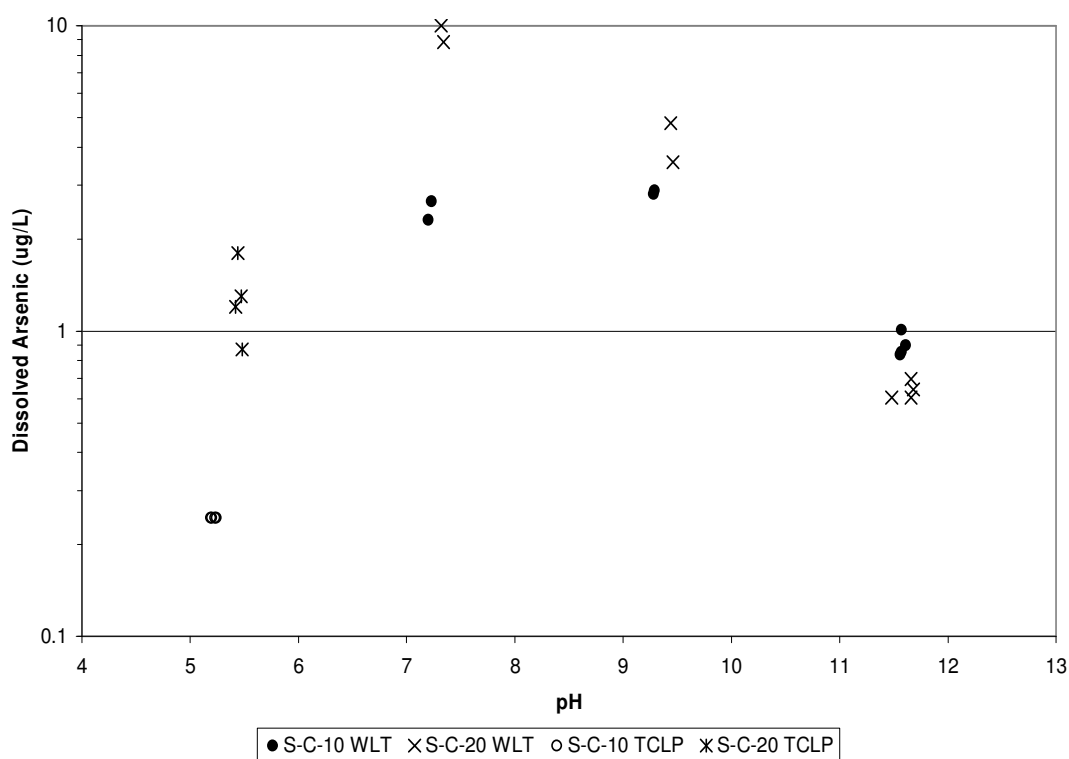


Figure 3.22: Effect of pH on arsenic concentrations for S-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Anionic repulsion could result in the higher concentrations seen in the pH range of 7-10. Highly alkaline conditions could cause the precipitation of As, leading to lower levels in the leachate as seen on the right side of the figure.

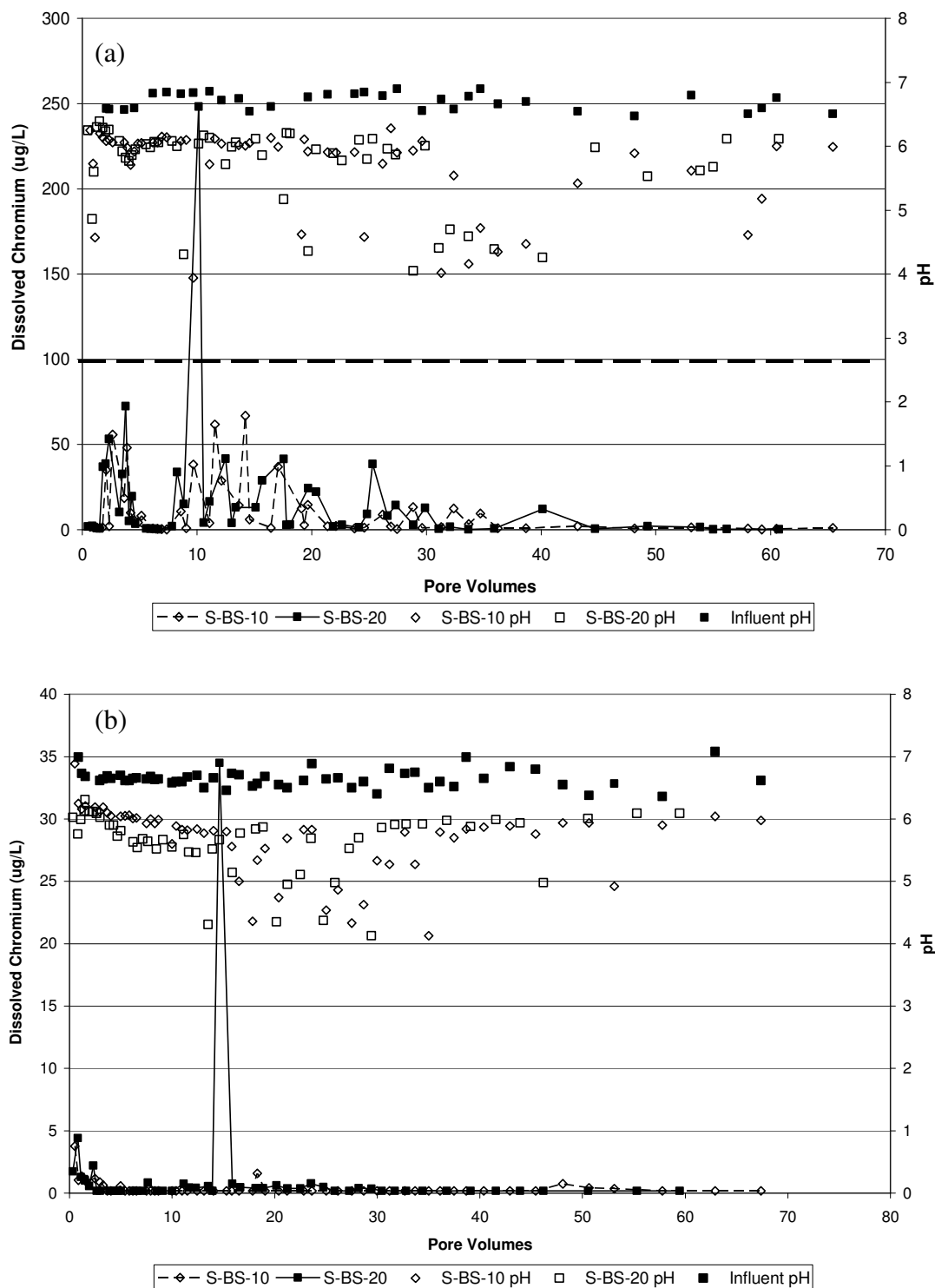


Figure 3.23: Chromium leachate concentrations from: (a) the 1st set of column leach test S-BS mixtures, and (b) the 2nd set of column leach test S-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.35 $\mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit. Dashed line represents EPA MCL of 100 $\mu\text{g/L}$.

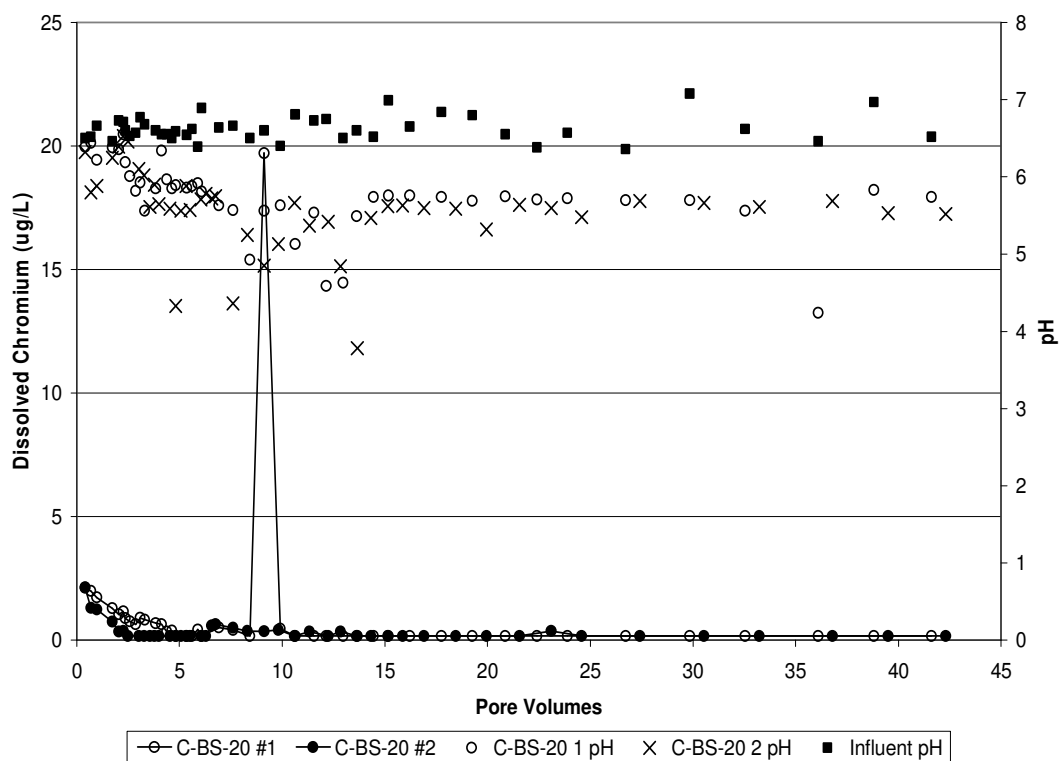


Figure 3.24: Chromium leachate concentrations from column leach test C-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations $< 0.35 \mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit.

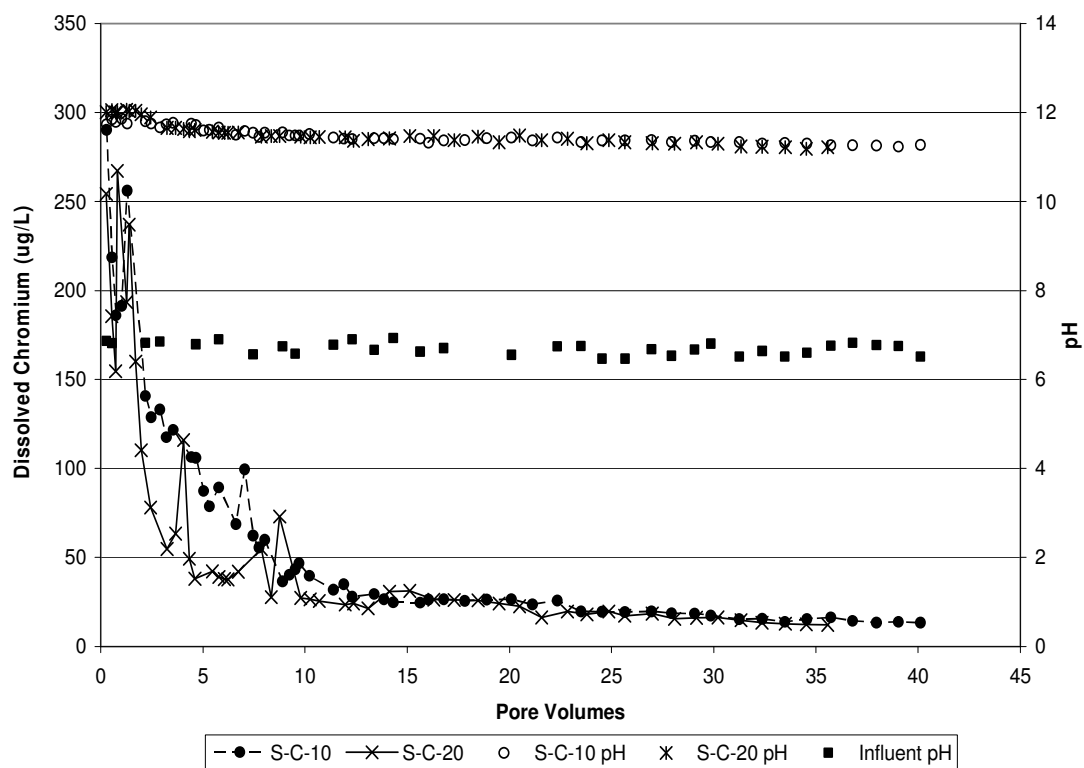


Figure 3.25: Chromium leachate concentrations from the column leach test S-C mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations $< 0.35 \mu\text{g/L}$ were reported as $\frac{1}{2}$ of the detection limit.

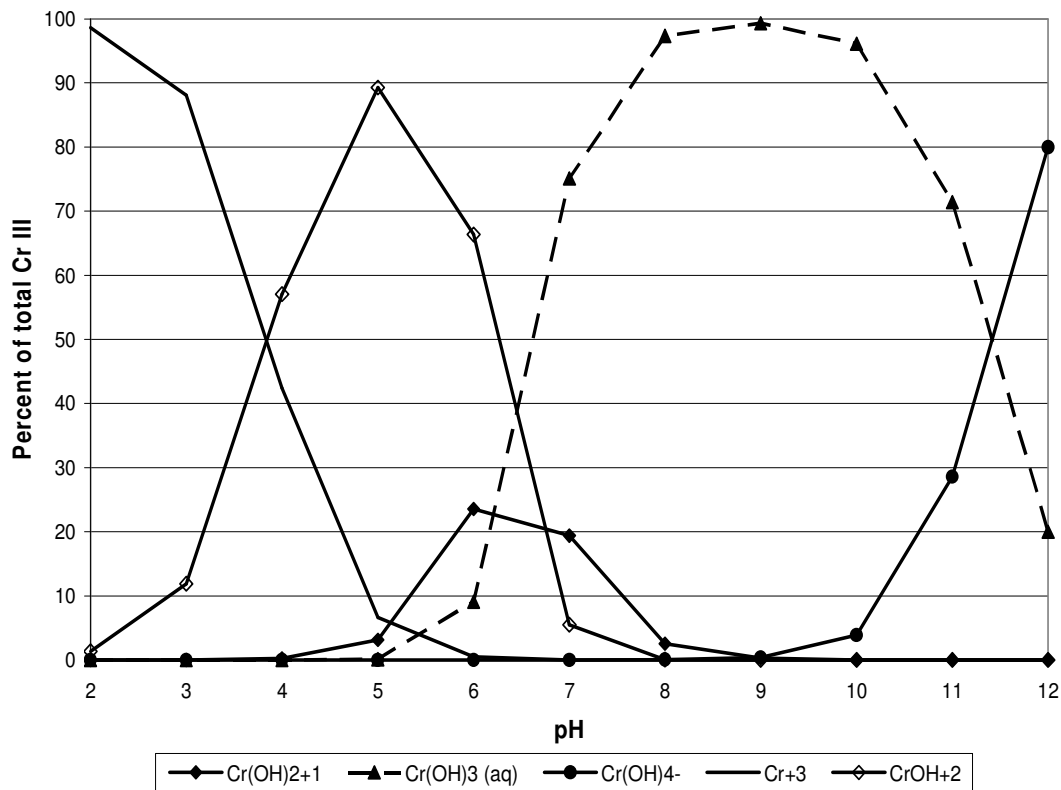


Figure 3.26: Effect of pH on Cr(III) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total Cr(III) concentration of 1 mg/L. As the pH increased from 2 to 12, the dominant Cr(III) species changes from Cr+3 to Cr(OH)4-.

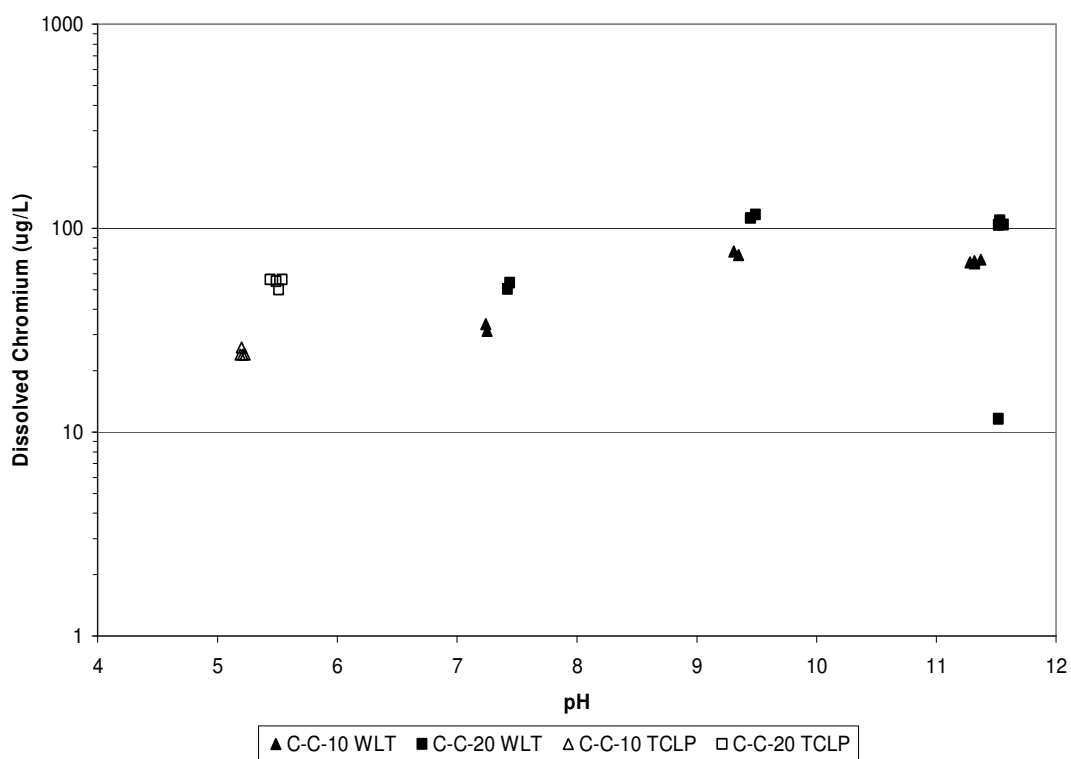


Figure 3.27: Effect of pH on leachate chromium concentrations for C-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Note the concentrations are within the same order of magnitude over a wide pH range from 5-10 and begin to approach and exceed the EPA MCL of 100 $\mu\text{g/L}$ at pH values above 9.

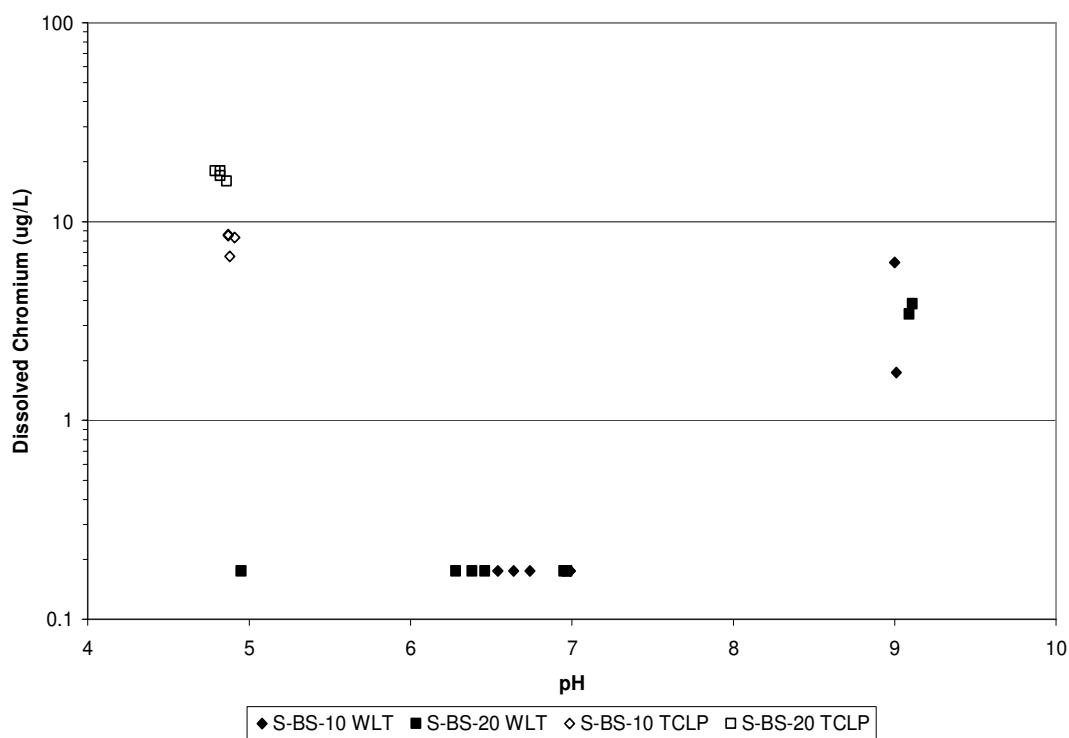


Figure 3.28: Effect of pH on leachate chromium concentrations for S-BS mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. The increased leaching of Cr at more acidic pH values (~5) and more alkaline pH values (~9) is similar to the solubility of Cr(III).

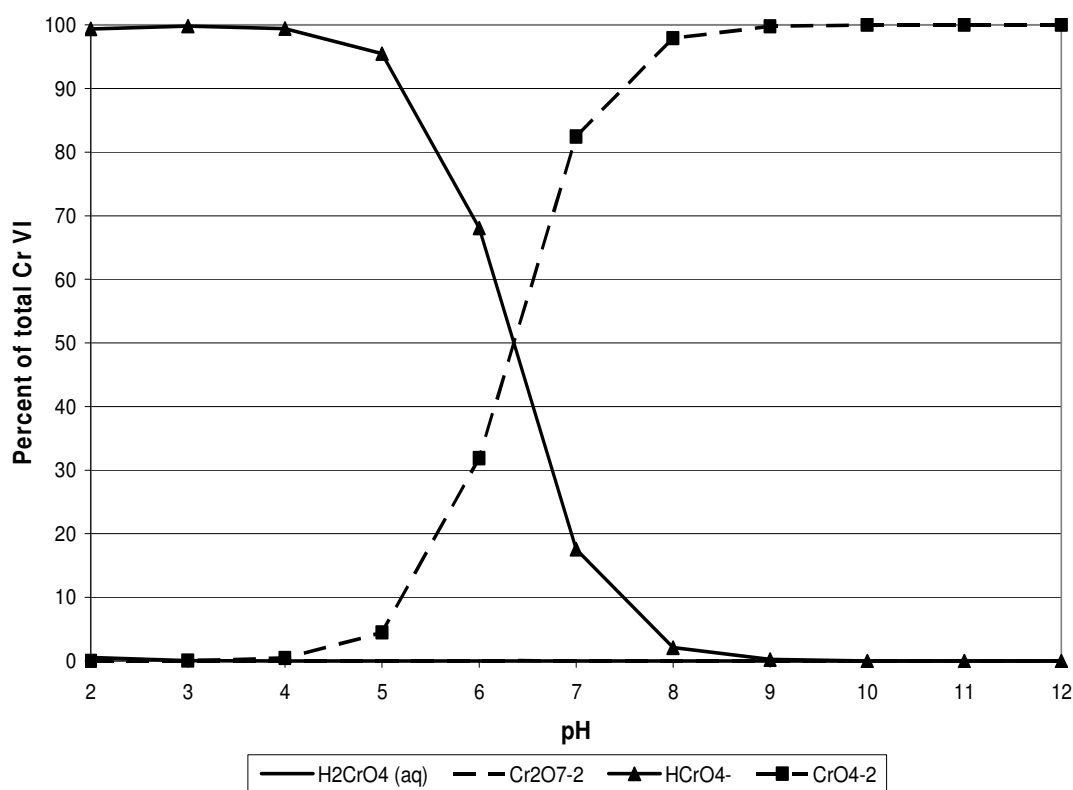


Figure 3.29: Effect of pH on Cr(VI) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total Cr(VI) concentration of 1 mg/L. In the pH range of 2-12, the dominant Cr(VI) species are anionic, which contributes to high solubility of Cr(VI) over a wide pH range.

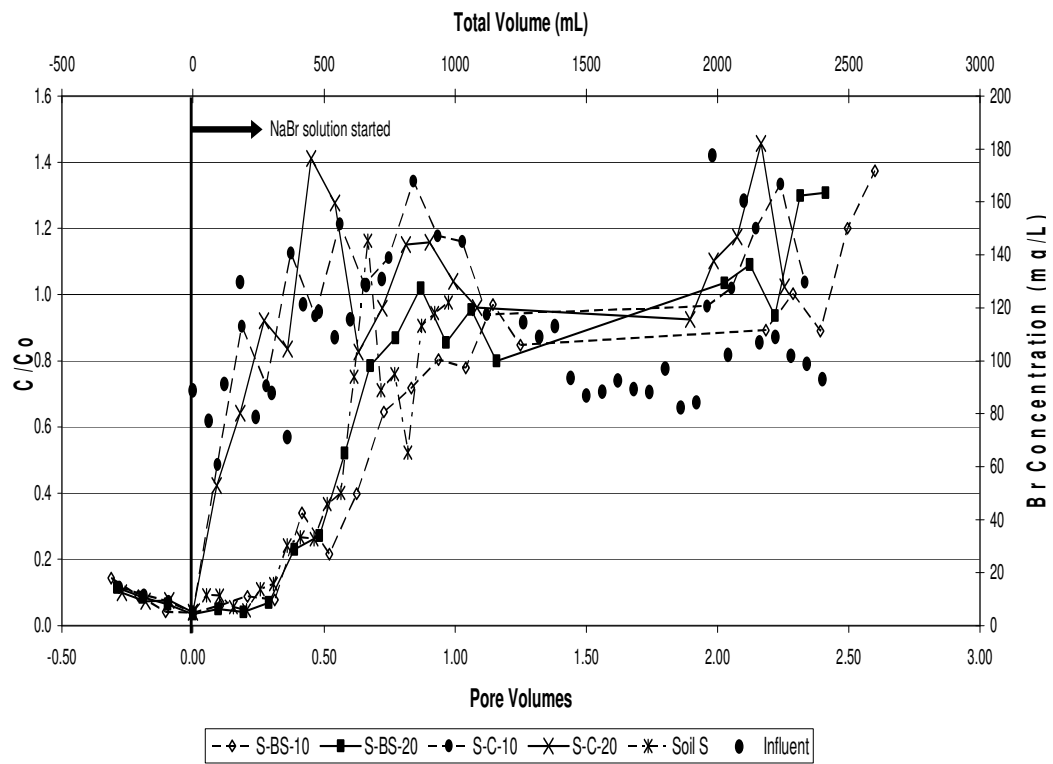


Figure 3.30: Breakthrough Curves from Tracer Study for 1st Set of Column Leach Tests. Influent bromide solution was 100 mg/L using NaBr. Negative numbers indicate conditions before switch to bromide step input.

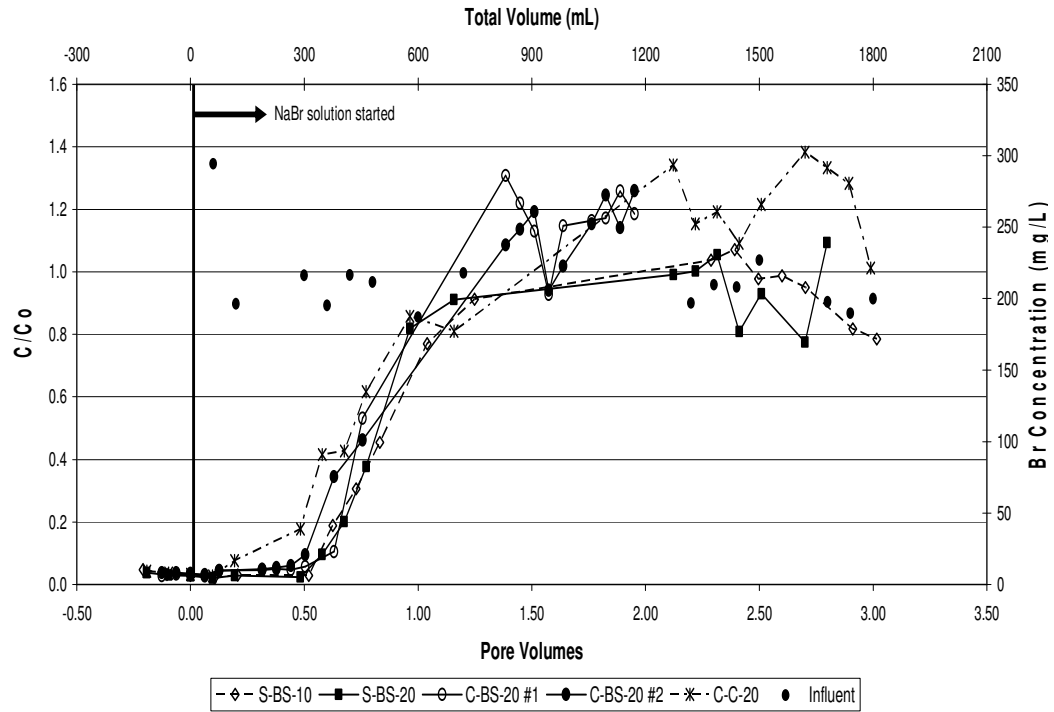


Figure 3.31: Breakthrough Curves from Tracer Study for 2nd Set of Column Leach Tests. Influent bromide solution was 250 mg/L using NaBr. Negative numbers indicate conditions before switch to bromide step input.

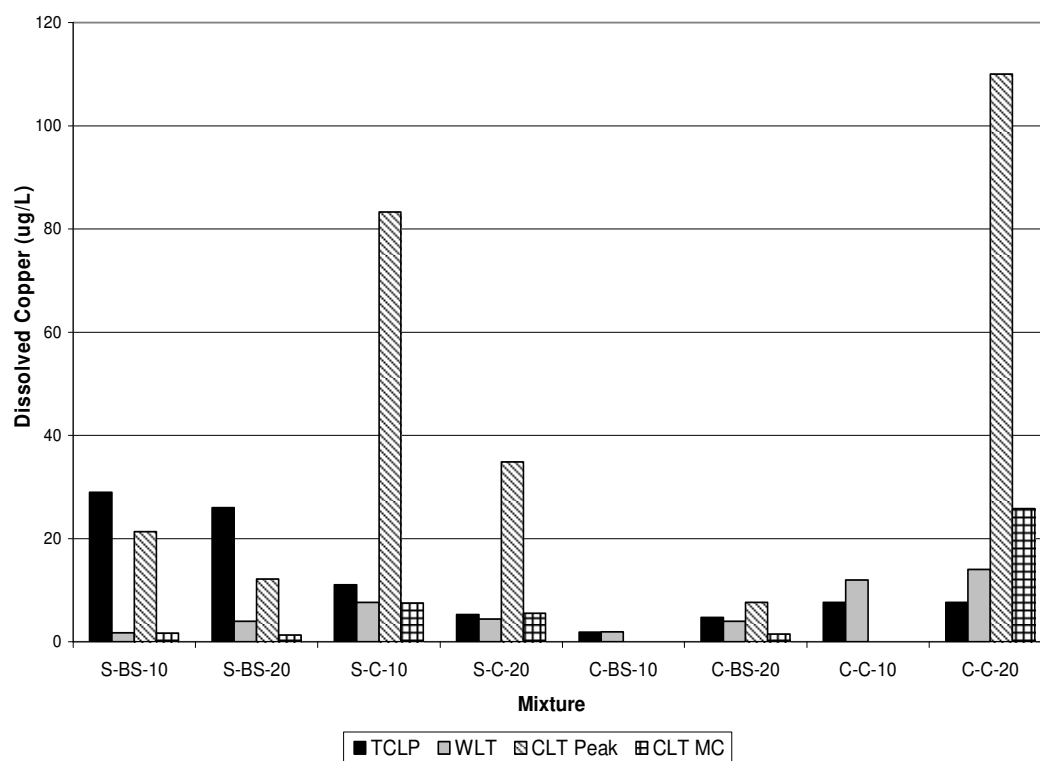


Figure 3.32: Comparison of copper leaching from water leach test, column leach test, and Toxicity Characteristic Leaching Procedure samples. C-BS-10 and C-C-10 mixtures were not tested using CLT methodology so no CLT data are reported in figure. Concentrations below detection limit are displayed as 0.

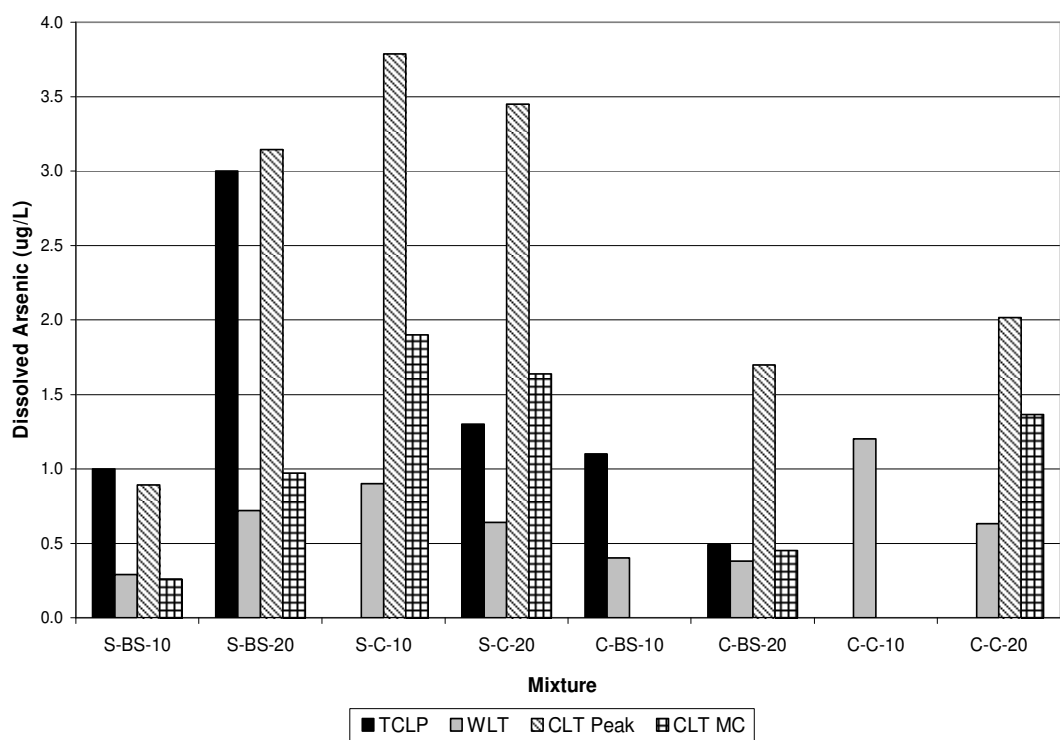


Figure 3.33: Comparison of arsenic leaching from water leach test, column leach test, and Toxicity Characteristic Leaching Procedure samples. C-BS-10 and C-C-10 mixtures were not tested using CLT methodology so no CLT data are reported in figure. Concentrations below detection limit are displayed as 0.

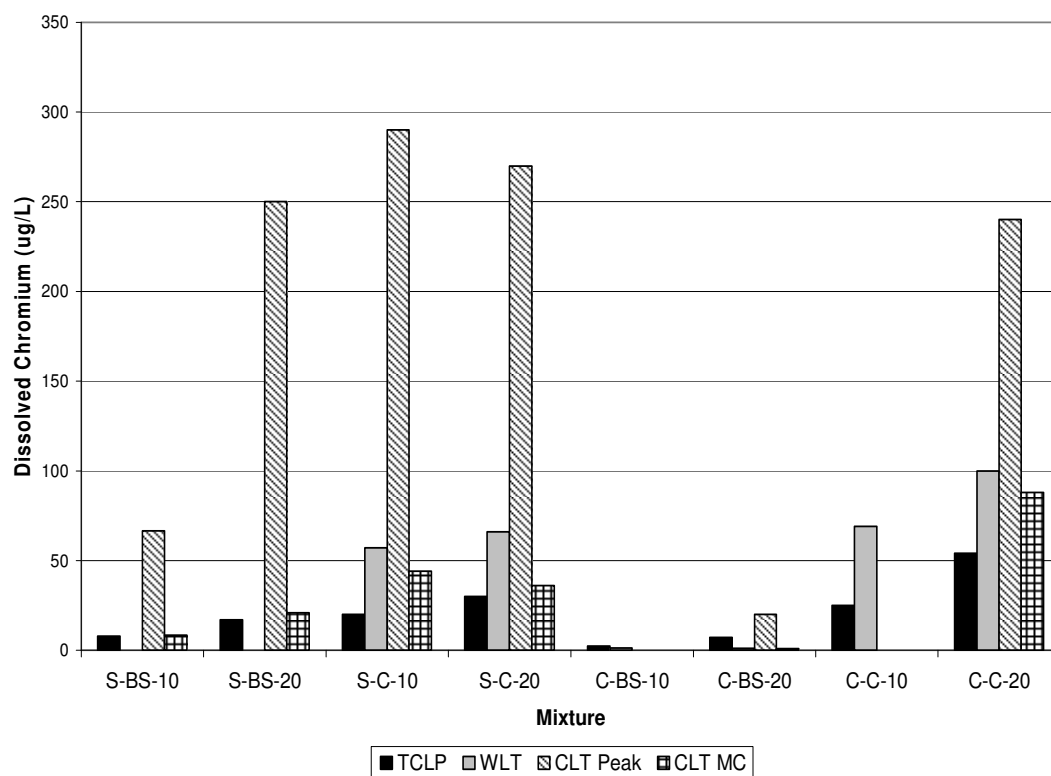


Figure 3.34: Comparison of chromium leaching from water leach test, column leach test, and Toxicity Characteristic Leaching Procedure samples. C-BS-10 and C-C-10 mixtures were not tested using CLT methodology so no CLT data are reported in figure. Concentrations below detection limit are displayed as 0.

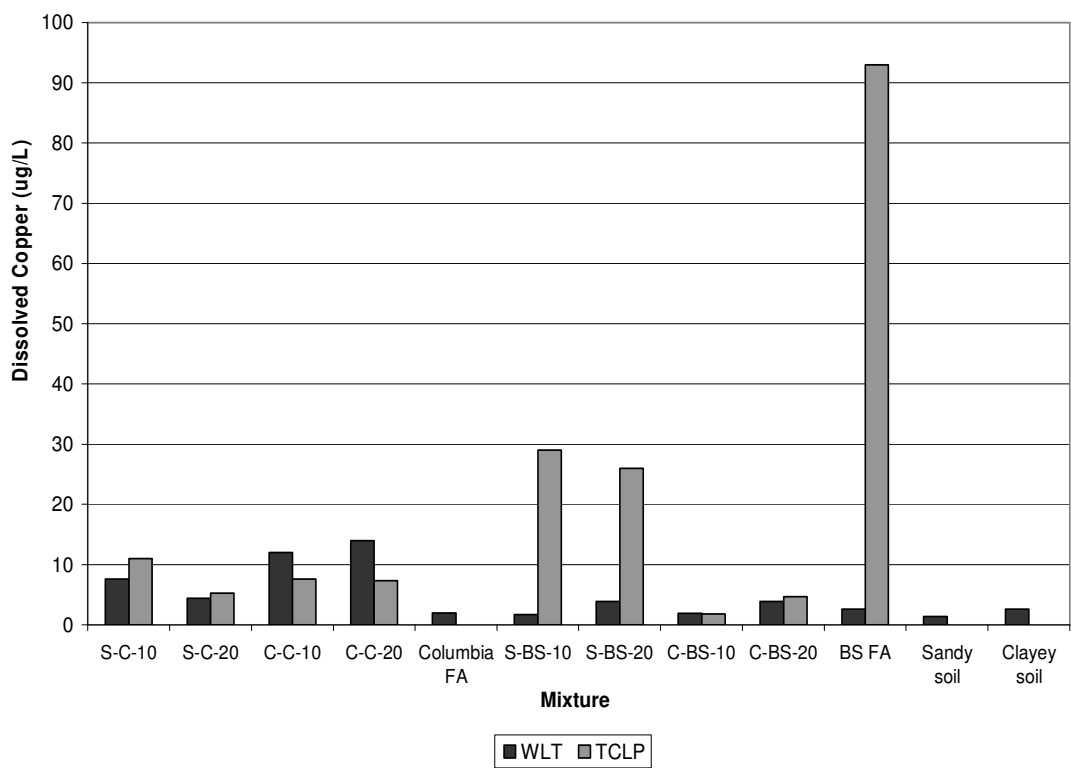


Figure 3.35: Comparison of water leach test and Toxicity Characteristic Leaching Procedure leachate copper concentrations. Concentrations below detection limit are displayed as 0.

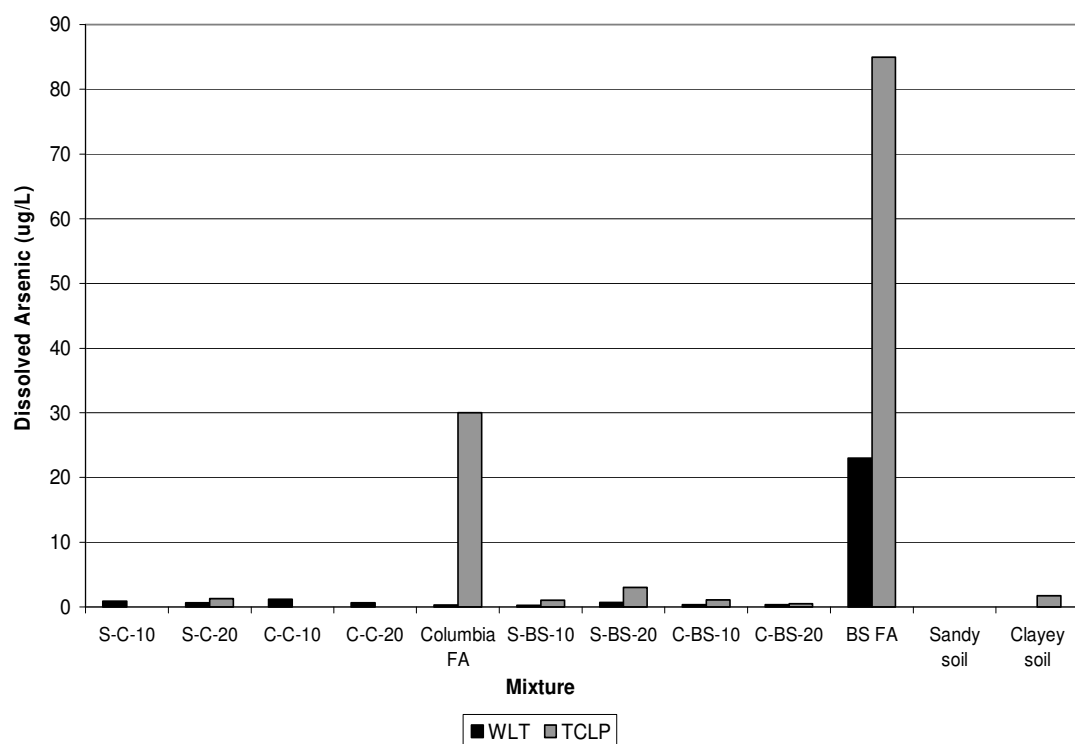


Figure 3.36: Comparison of water leach test and Toxicity Characteristic Leaching Procedure leachate arsenic concentrations. Concentrations below detection limit are displayed as 0. Note that no soil-fly ash mixture has arsenic concentrations that exceed the 10 $\mu\text{g/L}$ EPA MCL.

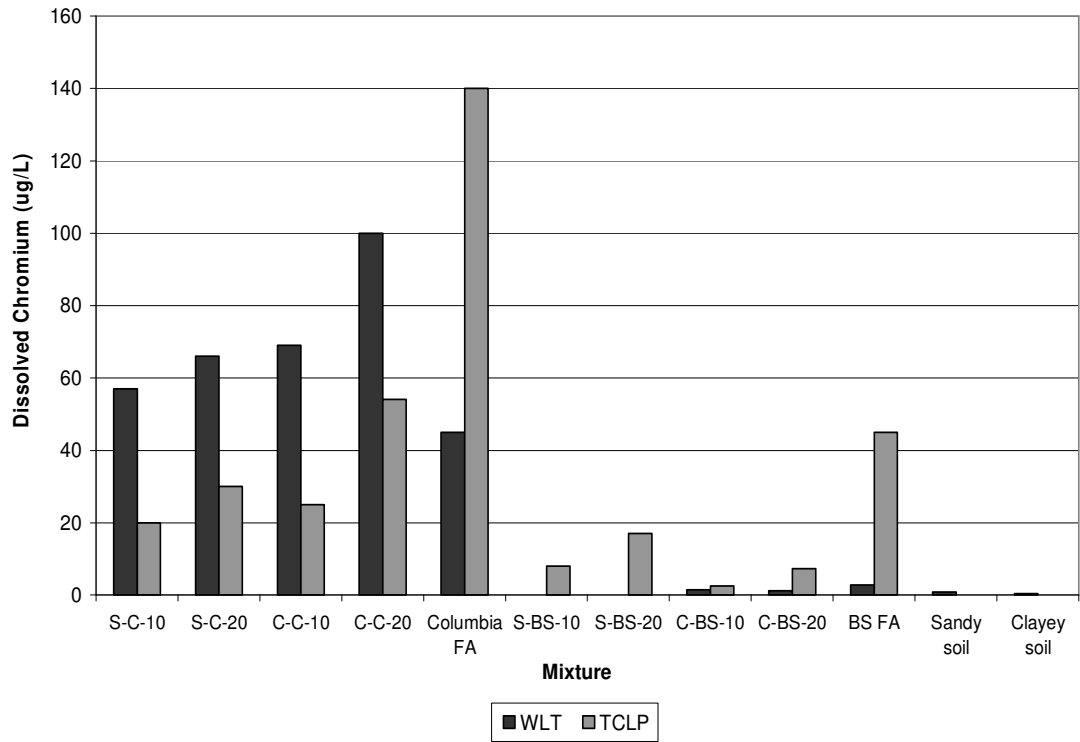


Figure 3.37: Comparison of water leach test and Toxicity Characteristic Leaching Procedure leachate chromium concentrations. Concentrations below detection limit are displayed as 0. As shown, the C fly ash mixtures on the left side have higher leachate chromium compared to the BS fly ash mixtures for both leaching tests, mainly a result of the highly alkaline pH conditions (~11.5) of the C fly ash.

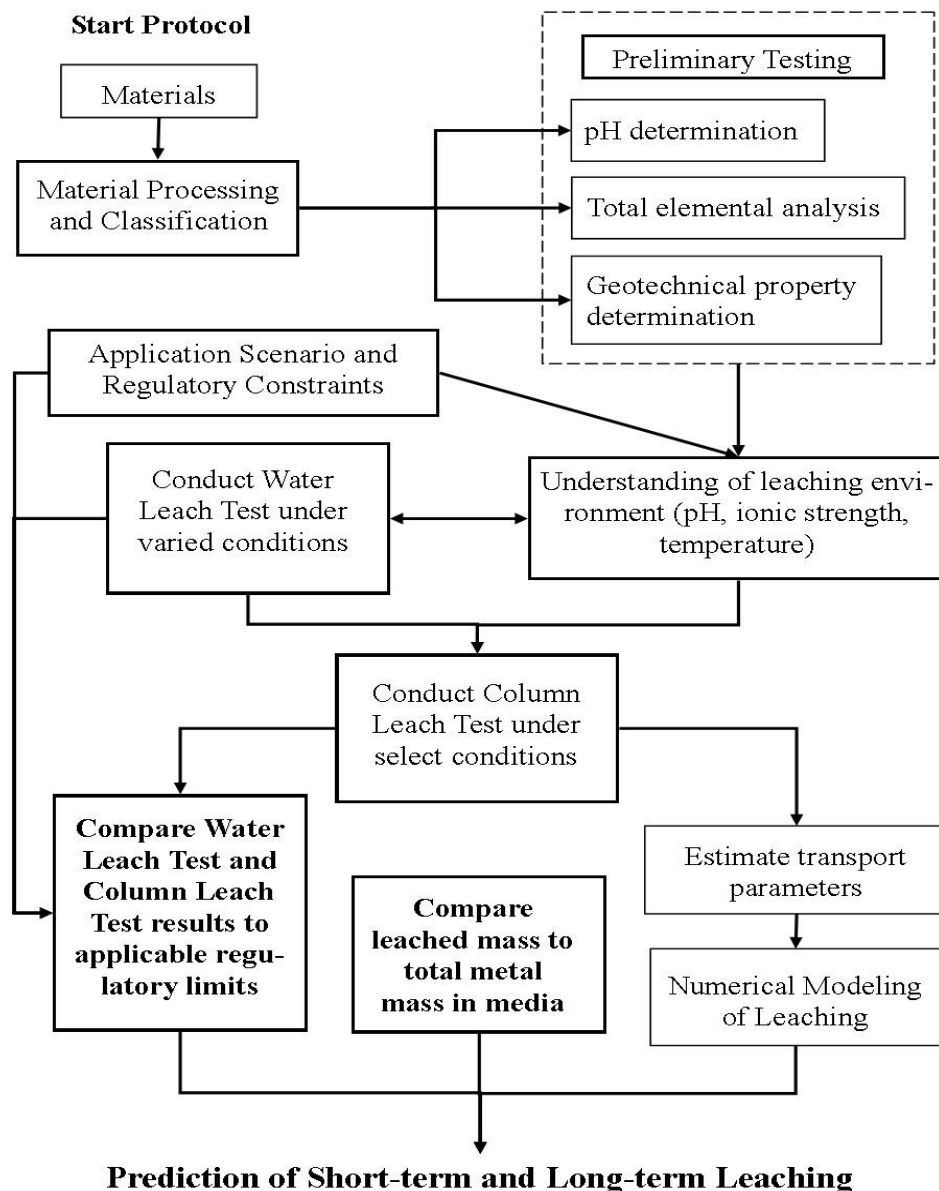


Figure 4.1: Summary of proposed leaching protocol. Preliminary testing provides foundation for conducting the water leach tests and column leach tests. Synthesis of different leaching test results provide evaluation of risks associated with heavy metal leaching. Additional preliminary testing, including L:S and contact time experiments, as well as numerical modeling, could be performed and incorporated depending on required level of detail and time frame.

Appendix B: Detailed Materials and Methods

B.1 Preparation and Determination of Extraction Fluids

The leaching solution for the CLT and WLT was prepared by dissolving 2.3376 grams sodium chloride (Fisher Scientific) in 2 liters of deionized water and mixing by magnetic stirrer for 5 minutes. The pH of each new batch was immediately measured, and adjusted to between 6.5 and 7 using 0.1 M NaOH prior to use in leaching tests.

Two different extraction fluids can be used in the TCLP test, depending on the sample properties. To determine which TCLP extraction fluid to use, 96.5 mL of deionized water were added to a beaker containing 5.0 grams of sample material, vigorously stirring for 5 minutes, and then measuring the pH. A measured pH of < 5 indicates that extraction fluid #1 should be used, whereas if the pH was > 5 , 3.5 mL of 1 N HCL are added and the mixture heated to 50°C for 10 minutes. If at this point the pH is < 5 , extraction fluid #1 is used, but if the pH is > 5 , extraction fluid #2 is used. In this work, extraction fluid #1 was appropriate in all cases. Extraction fluid #1 was prepared in large batches (5 liters) to maximize solution homogeneity. To create the solution, first 5.7 mL of glacial acetic acid (Fisher Scientific) was added to 500 mL of deionized water. Then 64.3 mL of 1N NaOH was added to the original solution, which was diluted to a final volume of 1 L with deionized water before mixing for 10 minutes. The pH of the solution was immediately measured and compared to the specified value of $4.93 \pm .05$ units. Generally, there was very close

agreement between the observed and required pH. In the case of discrepancies, 1 N NaOH was used to adjust the solution to the correct pH.

B.2 Preliminary Compaction Tests

The goal of these compaction tests was to determine the maximum dry unit weight and corresponding optimum water content. These values were needed in calculating the pore volume of each specific mixture for the CLTs. Compaction tests were performed on all soils and fly ash-soil mixtures according to ASTM D698. The compaction was done in three layers with 25 blows per layer from a standard compaction hammer in a circular motion. The dry unit weight of each mixture was calculated and plotted against water content to determine the water content that corresponded to the maximum unit weight. Two series of tests were performed: no delay and a 2 hour delay between the wetting of the mixture and compaction. Based on the compaction test results, the 2 hour delay had no significant impact on the maximum dry unit weights, and therefore was selected for use in the actual column specimen preparation. This delay simulated the delay often seen in actual compaction processes used on construction sites between the time the soil is moistened and mechanical compaction is applied.

B.3 Column Compaction Procedure

To prepare the compacted specimens for the CLTs, 10 kilograms batches of fly ash-soil mixture were mixed in five-gallon plastic buckets. The acrylic tubes were acid washed and then coated with a layer of silicone lubricant. The 100% silicone product

was not expected to influence the leaching results and would aid in the release of the compacted mixtures from the columns. After thorough mixing, sufficient water was added to the material to give a moisture content equal to 2% less than the OMC. Compaction of soil mixtures in the field typically is carried out dry of the OMC to account for additional wetting that occurs from precipitation. Subsequent mixing was done by hand and with a metal spoon to ensure the water was evenly distributed. After a period of two hours, the wetted fly ash-soil mixture was compacted in 8 equal layers, with 28 blows from a standard compaction hammer per layer in a circular motion. The procedure for compacting each column was determined from calculation of total energy (13750 ft-lbf/ft³) delivered to the compacted media adjusted for the taller column height compared to the standard 4 inch tall Proctor compaction mold.

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